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PATENT ABSTRACTS OF JAPAN

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(54) DOUBLE PACKAGE

(57)Abstract:

PURPOSE: To preserve cooked food which contains moisture and oil in its ingredients and which is likely to get moldy under such conditions that mold is difficult to be generated while appropriate moisture is maintained inside the food.

CONSTITUTION: An individual package (A) is a double package sealed by an oxygen permeability adjustable laminated film comprising a base material made of biaxial oriented polyethylene with a density of 0.930g/cm2 or more and oxygen permeability of 4,000 to 12,000cc/m2.day.atm and a polyolefin sealant layer selected from a group including low density polyethylene, linear low density polyethylene, ethylene-polyvinyl acetate copolymer, ethylene-acrylic acid copolymer, ethylene-ethylacrylate copolymer and ionomer. Using the base material which has been subjected to electron beam application with irradiation of 5 to 30 Mrad provides a package wherein preferred oxygen permeability can be adjusted.

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(54)【発明の名称】　二重包装体

(57)【要約】　（修正有）
【目的】　成分中に水分や油分を含有した黴の発生しやすい加工食品を、内部に適度な水分を保持したまま、黴の発生しにくい条件で保存し得る包装体の提供。
【構成】　該個装(A)が、密度が０．９３０ｇ／ｃｍ³以上、酸素透過度が４，０００ないし１２，０００ｃｃ／ｍ²・ｄａｙ・ａｔｍの二軸延伸したポリエチレンからなる基材と、低密度ポリエチレン、線状低密度ポリエチレン、エチレン－酢酸ビニル共重合体、エチレン－アクリル酸共重合体、エチレン－エチルアクリレート共重合体、アイオノマーからなる群より選ばれたポリオレフィン系シーラント層との酸素透過度調節積層フィルムでシール包装された二重包装体。また、基材として、照射度５ないし３０Ｍｒａｄに電子線照射されたものを使用することによって好適な酸素透過度が調節された包装体となる。

1

【特許請求の範囲】

【請求項1】 水分または油分含有食品を密封包装した個装(A)と、酸素吸収剤を収納した個装(B)を同時に密封包装した外装袋(C)からなる二重包装体において、該個装(A)が、密度が0．930g／cm³以上、酸素透過度が4，000ないし12，000cc／m²・day・atmの二軸延伸したポリエチレンからなる基材と、低密度ポリエチレン、線状低密度ポリエチレン、エチレン－酢酸ビニル共重合体、エチレン－アクリル酸共重合体、エチレン－エチルアクリレート共重合体、アイオノマーからなる群より選ばれたポリオレフィン系シーラント層との酸素透過度調節積層フィルムでシール包装されたものであることを特徴とする二重包装体。

【請求項2】 前記ポリオレフィン系シーラント層が、基材と同等以上の酸素透過度を有するものである請求項1記載の二重包装体。

【請求項3】 前記外装袋(C)が、ガスバリヤー性のフィルムまたは積層フィルムによって密封包装されている請求項1または2記載の二重包装体。

【請求項4】 前記基材の、蛍光配向法による配向係数が、0．1≦l≦0．90，0．1≦m≦0．90，0．2≦n≦0．80である請求項1ないし3のいずれか1項記載の二重包装体。

【請求項5】 前記基材が、照射度5ないし30Mradに電子線照射されたものである請求項1ないし4のいずれか1項記載の二重包装体。

【請求項6】 前記基材とシーラント層の間にさらに低密度ポリエチレンの層を設ける請求項1ないし5のいずれか1項記載の二重包装体。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、二重包装体に関するものであって、より詳しくは、内容物として、成分中に水分または油分を含有する黴の発生し易い食品を密封包装した個装(A)と、酸素吸収剤を収納した個装(B)を同時に密封包装した外装袋(C)からなる二重包装体であって、該個装(A)の酸素透過度を黴の発生を抑制するに好適な条件に調整した二重包装体に関する。

【0002】

【従来の技術】各種の加工食品が、衛生上の見地から、あるいは保存性を高める目的で、フィルム状包装体によって包装され、販売に供されていることは良く知られている。加工食品の中でも、成分中に水分や油分を含有するものは、酸素の影響によって酸化しやすく、かつ、ヒートシール後のUV殺菌によっても、包装体内の食品中に殺菌されずに残存する黴菌がある場合には、この黴菌が酸素と接触することによって更に繁殖し、食品としての意味を失うに至ることがある。

【0003】したがって、このような食品の包装体においては、通常、内容物である食品の保存性を高める目的

2

で、包装体内に、エージレスなどの商品名で知られている酸素吸収剤を収納した通気性の個装（本願明細書では、以下、これを「個装（B)」ということがある）を収納することが行われている。また、包装体を構成するフィルムの素材として、酸素の透過を抑制するために、ガスバリヤー性に優れた各種の積層フィルムを用いることなどが試みられているが、その効果も必ずしも十分なものとは言いがたく、とくに内容物が、餅、ケーキ類、または和菓子などのように、わずかな酸素の影響によって腐敗や黴の発生が促進されるものにあっては、十分に満足し得る包装体は得られていない。

【0004】従来、このような食品の外装袋用の包装体の素材としては、ナイロンの表面に塩化ビニリデン樹脂をコーティングしたフィルムを基材としたものが広く用いられているが、この包装体においても、そのなかに収納する、食品を包装した個装(A)におけるヒートシール後のUV殺菌時に死滅しなかった黴菌が、初期封入酸素によって成育し、内容物に付着して、商品価値を損ねてしまうという事故が相次いでいる。

【0005】このように、食品を密封包装した個装(A)と酸素吸収剤を収納した個装(B)を内蔵した食品包装体においては、包装体内の酸素が酸素吸収剤に吸収されるほど、当然、包装体内の酸素濃度は低くなり、包装体内の食品のシェルフライフは長くなる。この際、酸素吸収剤に吸収される酸素の量は、個装(A)包装体を構成するフィルムの酸素透過性が大きいほど多くなり、シェルフライフを伸ばす効果が大きいものとなる。

【0006】しかしながら、その反面、酸素透過性が余り大きいと、これと相関して水蒸気透過性も大きくなり、この場合には、個装(A)を外装袋(C)に充填するまでの間に外気の水蒸気が個装(A)内に透過し、食品に結露し、とくに、餅、和菓子あるいは洋菓子などの加工食品においては、黴の発生を促進し、食品の寿命を短くする結果を招く。さらに、例えば、切り餅などの場合は40％程度の水分を保持していることが製品として好ましいものとされているが、個装(A)の酸素透過度が大き過ぎると、個装(A)内の食品にとって当然保持されていなければならない好ましい範囲の水分以上の水分までを蒸散することになり、この場合は、食品が固くなってしまい、商品価値を著しく損なうことになる。

【0007】

【発明が解決すべき課題】そこで、本発明の目的は、成分中に水分あるいは油分を含有する加工食品を、必要な水分を保持しつつ、内部の酸素を好適に放出させて、最も黴の発生しにくい条件になるように包装した二重包装体を提供することにある。

【0008】

【課題を解決するための手段】本発明は、前記目的を達成するために提案されたものであり、その特徴とするところは、食品を包装した個装(A)と、酸素吸収剤を収納

3

した個装(B) とを共に包装する外装袋(C) からなる二重包装体の、該個装(A) を構成する積層フィルムを特定の物性を有するポリマーからなる層によって構成する点にある。

【０００９】すなわち、本発明によれば、水分または油分含有食品を密封包装した個装(A) と、酸素吸収剤を収納した個装(B) を同時に密封包装した外装袋(C) からなる二重包装体において、該個装(A) が、密度が０．９３０ｇ／ｃｍ³ 以上、酸素透過度が４，０００ないし１２，０００ｃｃ／ｍ² ・ｄａｙ・ａｔｍの二軸延伸したポリエチレンからなる基材と、低密度ポリエチレン、線状低密度ポリエチレン、エチレン－酢酸ビニル共重合体、エチレン－アクリル酸共重合体、エチレン－エチルアクリレート共重合体、アイオノマーからなる群より選ばれたポリオレフィン系シーラント層との酸素透過度調節積層フィルムでシール包装されたものであることを特徴とする二重包装体が提供される。この二重包装体の外装袋(C) は、当然のことながら、ガスバリヤー性のフィルムまたは積層フィルムによる密封包装によって構成されていることが必要であり、それによって、個装(A) と外装袋(C) の間に存在する酸素がまず個装(B) の酸素吸収剤によって吸収され、次いで、個装(A) の壁面を通して透過してくる酸素も該酸素吸収剤に吸収されることにより、個装(A) 内の食品が黴の発生しにくい条件に保持されることになる。

【００１０】また、本発明によれば、前記個装(A) の基材が、蛍光配向法による配向係数が、０．１≦ｌ（ｴﾙ）≦０．９０，０．１≦ｍ≦０．９０，０．２≦ｎ≦０．８０である二軸延伸ポリエチレンによって構成される二重包装体が提供される。さらに、本発明によれば、前記個装(A) の基材が照射度５ないし３０Ｍｒａｄに電子線照射されたものである酸素透過度を調節した二重包装体が提供される。さらにまた、本発明によれば、個装(A) における前記基材とシーラント層の間にさらに低密度ポリエチレンの層を設けることによって、ラミネート強度とヒートシールが一層優れた個装が得られ、酸素透過度調節作用が一層優れた二重包装体が提供される。

【００１１】

【発明の具体的説明】本発明者らは、外装袋(C) 内に酸素吸収剤を収納した個装(B) と共に、成分中に水分や油分を含有する加工食品の個装(A) を収納した二重包装体において、黴の発生を好適に抑制する条件を試行錯誤により求めていたところ、包装後３日以内に個装(A) 内の酸素濃度が０．１％以下となる適度な酸素透過性を有するフィルムが、該二重包装体の個装(A) 用フィルム素材としてに好適に使用し得るという知見を得て、本発明を完成した。

【００１２】成分中に水分や油分を含有する加工食品を密封包装した個装(A) と酸素吸収剤を収納した個装(B) を共に外装袋(C) に収納する本発明の包装体における最

4

大の技術的特徴は、個装(A) を構成する積層フィルムの基材として特定の物性を有するポリマーを使用する点にある。つまり、本発明の最大の技術的特徴は、前記二重包装体において、個装(A) を構成する積層フィルムの基材として、密度が０．９３０ｇ／ｃｍ³ 以上、モコン法で測定した酸素透過度が４，０００ないし１２，０００、好ましくは５，０００ないし１０，０００ｃｃ／ｍ² ・ｄａｙ・ａｔｍの二軸延伸したポリエチレンフィルムないしシートを用い、シーラント層として、低密度ポリエチレン、線状低密度ポリエチレン、エチレン－酢酸ビニル共重合体、エチレン－アクリル酸共重合体、エチレン－エチルアクリレート共重合体、アイオノマーからなる群より選ばれた基材と同等以上の酸素透過度を有するポリオレフィン系シーラント層ををを用いたことにある。この基材の酸素透過度の規定は、本発明者らの度重なる実験の結果として見いだされたもので、酸素吸収剤を収納した個装(B) を内蔵する本発明の二重包装体にあっては、酸素吸収剤の酸素吸収速度を適度なものに調整するために重要であり、この範囲を超えても、あるいはこの範囲より少なくても、内容物のシェルフライフを長くすることはできない。

【００１３】＜個装(A) の基材＞本発明の二重包装体における個装(A) の基材としては、密度が０．９３０ｇ／ｃｍ³ 以上、酸素透過度が４，０００ないし１２，０００、好ましくは５，０００ないし１０，０００ｃｃ／ｍ² ・ｄａｙ・ａｔｍの二軸延伸したポリエチレンのフィルムないしシートが使用される。前記基材の二軸延伸の程度は、蛍光配向法による配向係数で表され、０．１≦ｌ（ｴﾙ）≦０．９０，０．１≦ｍ≦０．９０，０．２≦ｎ≦０．８０であることが重要である。基材の配向係数が、前記の範囲をはずれる場合には、酸素透過度が本発明が目的とする、４，０００ないし１２、０００ｃｃ／ｍ² ・ｄａｙ・ａｔｍの条件を満たさないものとなり、内容物の保存性において劣ったものとなる。

【００１４】蛍光配向法とは、蛍光性分子が発する蛍光の偏光特性の角度分布から蛍光性分子の分子配向の状態を求める方法であり、蛍光性分子を高分子固体非晶域に拡散導入することにより、高分子非結晶鎖の配向状態を求める方法である。蛍光偏光成分強度は、２つの偏光板Ｐ１、Ｐ２を平行にした時をＩ∥、直交にした時をＩ⊥とする。これらの蛍光偏光成分強度の角度分布は、試料Ｏの回転角ωの関数として求まる。

$$I\ (\omega) = K\Phi\ (l\cos^4\omega + m\sin^4\omega + n) \quad l+m+n=1$$

において、

ｌ：製膜形成方向に平行な方向への配向

ｍ：製膜形成方向に直角な方向への配向

ｎ：面内無配向

をそれぞれ示すパラメータである。

ｌ＝ｍ＝０とすれば、面内無配向を

5

m＝n＝0とすれば、完全1軸配向を
l＝m，n＝0とすれば、完全直交2軸配向を、それぞれ示す。

【0015】また、本発明の二重包装体における個装(A)の基材を構成するポリエチレンは、電子線（EB）を照射することによって、前記酸素透過度が一層好適な範囲のものに調整される。電子線の照射は、自体公知の照射装置によって行うことができ、照射量は5ないし30Mrad、好ましくは7ないし20Mrad、とくに好ましくは10ないし15Mradである。

【0016】＜個装(A)のシーラント層＞本発明の二重包装体を構成する個装(A)のシーラント層としては、低密度ポリエチレン、線状低密度ポリエチレン、エチレン－酢酸ビニル共重合体、エチレン－アクリル酸共重合体、エチレン－エチルアクリレート共重合体、アイオノマーからなる群より選ばれたポリオレフィン系シーラントが選択的に使用され、なかでも、低密度ポリエチレン及びエチレン－アクリル酸共重合体が好適に使用される。個装(A)全体の酸素透過度を前述した好適なものに保つには、シーラント層の酸素透過度は前記基材の酸素透過度と同等以上であることが必要である。

【0017】＜個装(A)の中間層＞本発明においては、個装(A)の前記基材とシーラント層の間に、さらに中間層を設けることもできる。中間層のポリマーとしては、シーラント層を構成するポリマーと同種のものが好ましく、メルトインデックスが2．0ないし12．0、密度が0．917以上0．930未満の低密度ポリエチレンが好適に使用される。この中間層も、当然前記シーラント層と同様に、酸素透過度が基材の酸素透過度と同等以上のものであることが必要である。

【0018】中間層がシーラント層と同種のポリマーで構成される場合には、シーラント層と中間層の合計厚みは、基材とシーラント層のみからなる積層フィルムのシーラント層と同程度の厚みに形成することが好ましい。つまり、例えば、基材とシーラント層のみから構成される場合は、HDPE 20μ／LDPE 30μであれば、3層構造の場合は、HDPE 20μ／LDPE 15μ／LDPE 15μとして形成されることが好ましい。30μのシーラント層を設けるのと、同種のポリマーからなる15μの層を2層設けるのとでは、全体の層の厚みは同じであるが、15μの層を2層設けることにより、中間層は基材との接着力向上に寄与し、シーラント層はヒートシールの向上に寄与するという包装体の製法上のメリットがあり、したがって、得られる包装体もこの点の利点を有したものとなり、この方が、好ましいことが理解されるであろう。

【0019】＜個装(A)の厚み比構成＞本発明の包装体における個装(A)は、前述したように、基材／シーラント層、または基材／中間層／シーラント層から構成されるものであるが、各層の厚みは、基材／シーラント層から構成される場合には、15μないし30μ／20μないし50μ、とくに15μないし20μ／25ないし30μが好ましい。また、包装体が基材／中間層／シーラント層から構成される場合には、15μないし30μ／10μないし25μ／10μないし30μ、とくに15μないし20μ／10μないし15μ／10μないし15μが好ましい。

6

【0020】＜外装袋（C)＞本発明の外装袋(C)としては、ガスバリヤー性に優れたフィルムまたは積層フィルムが使用され、例えば、ポリ塩化ビニリデンをコーティングしたナイロン、ビニルアルコール含量が50ないし70モル%のエチレン－ビニルアルコール共重合体、またはアルミ箔などを層構成材料として使用するものが好ましく例示される。

【0021】＜積層フィルムの製法＞本発明の個装(A)を構成する積層フィルムは、自体公知のラミネート装置によって容易に製造することができる。例えば、まず、エクストルーダーからポリエチレンをシングル押出しによって基材を形成し、この基材の上にシーラント層を単独でラミネートするか、またはシーラント層と中間層をタンデム押出しによってラミネートする方法が例示される。

【0022】＜包装体の製法＞本発明の個装(A)を構成する酸素透過度調節包装体は、前記積層フィルムを用いて、包装する内容物の形状に応じたシールを行うことによって製造される。例えば、本発明の酸素透過度調節包装体の好適な内容物である餅（切り餅）の場合には、センターシールを行った後、フィルムの上下（ボトム）をシールして、合計3か所をシールすることによって、包装体（個装（A））が得られる。シール温度は、シーラント層を構成するポリマーによっても相違するが、通常、センターシールを150ないし220℃で行い、ボトムシールを120ないし150℃で行うことが好ましい。

【0023】

【発明の効果】本発明によれば、成分中に水分や油分を含有した加工食品を、内容物の水分を過剰に蒸散させることなく、かつ、酸素透過度を適度な範囲に調整した積層フィルムによって個装(A)を形成し、これを酸素吸収剤を収納した個装(B)と共に外装袋(C)によって包装することによって、例えば、切り餅などのように、適度の水分を含有していることが必要な加工食品においても、黴の発生を著しく抑制した包装体が提供される。

【0024】

【実施例】本発明を以下に示す実施例及び比較例をもって説明する。個装の基材の種類、厚み、配向度、電子線（EB）照射の量、及びシーラント層の種類、厚みを、それぞれ表に示したようにして、ラミネートフィルムを調製した。次いで、このラミネートフィルムを用いて、製造後3日間冷蔵熟成してカットした切り餅を、センターシールを160℃、上下のボトムシールを150℃でシール包装し、その保存適性を評価した。包装体の評価

7

中、○は、２５℃、－５０％、４日間の条件で徴の発生を生じなかったもの、△は、同条件で約１０ないし５０％の確率で徴が発生したもの、×は、同条件で５０％以

8

上の確率で徴が発生したもの、を表す。（なお、No 8は、水蒸気透過が大き過ぎ内容品の品質を損なった。）

【表１】

No	基材				シーラント層		酸素透過度 cc/m² day 1atm		包装体評価
	種類	厚み μ	配向度 ℓ m n	EB照射 Mrad	種類	厚み μ	外層	積層体	
1	HDPE	15	0.05 0.05 0.9	——	LDPE	30	12400	11500	×
2	HDPE	15	0.1 0.1 0.8	15	LDPE	30	4400	3900	△
3	HDPE	15	0.3 0.3 0.4	——	LDPE	30	4400	4000	△
4	HDPE	15	0.3 0.3 0.4	5	LDPE	30	5000	4800	○
5	HDPE	15	0.3 0.3 0.4	10	LDPE	30	6000	5800	○
6	HDPE	15	0.3 0.3 0.4	15	EAA	30	6000	5700	○
7	HDPE	15	0.3 0.3 0.4	15	PP	30	6000	3800	△
8	HDPE	15	0.3 0.3 0.4	30	LDPE	30	12000	11300	△
9	HDPE	16	0.4 0.35 0.25	15	LDPE	30	4300	3900	△
10	HDPE	20	0.3 0.25 0.45	15	LDPE	30	5400	5100	○
11	LDPE	15	0.25 0.25 0.5	15	LDPE	30	12600	12000	×
12	PP	20	0.2 0.2 0.6	——	LDPE	30	2900	2600	×
13	Nylon-6	15	0.3 0.2 0.5	——	LDPE	30	40	40	×
14	Nylon-6	15	0.3 0.2 0.5	36	LDPE	30	50	50	×
15	PET	12	0.2 0.2 0.6	——	LDPE	30	60	60	×
16	PET	12	0.2 0.2 0.6	35	LDPE	30	45	45	×
17	EVOH	15	0.05 0.05 0.9	35	LDPE	30	2	3	×

表中、HDPEとしては、密度0.955g/cm³のポリエチレン、LDPEとしては、密度0.920g/cm³のポリエチレンを使用した。

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(54) Title: A METHOD FOR THE LONG-TERM PRESERVATION OF MEAT AND THE MEAT PROCESSED THEREBY

(57) Abstract

A method for preserving meat and the meat processed thereby is disclosed. The method includes the steps of exposing raw meat to an atmosphere consisting essentially of carbon monoxide and maintaining the meat in a sealed container to maintain color and freshness while retarding bacterial growth.

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A METHOD FOR THE LONG-TERM PRESERVATION OF MEAT AND THE MEAT PROCESSED THEREBY

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

The present invention relates to a method for preserving raw meat and more specifically relates to a method for preserving raw meat by exposing the meat to an atmosphere consisting essentially of carbon monoxide.

BACKGROUND ART

It is well known in the meat processing industry that from the time animals are slaughtered, measures must be taken to preserve the meat and prevent it from becoming rancid or spoiled. The measures to preserve raw meat must be implemented and carried through from the time the animal is first slaughtered through the time the meat is purchased and ultimately consumed by the purchaser.

Historically, preservation of the freshness or quality of the meats has been practiced for hundreds, if not thousands of years. Early preservation techniques of meat took the form of drying or "jerking" meat and packing or storing

cuts of meat in salt. This method, while somewhat effective for preserving meat and keeping it from becoming spoiled, had many drawbacks not the least of which was the incorporation of large amounts of salt into meat slated for human consumption.

The use of additives or preservatives such as nitrates and nitrites to meats is another common technique for preserving meat over time. However, there is ever increasing evidence that such additives may have harmful, even carcinogenic drawbacks. These drawbacks detract from the use of these compounds as mechanisms for the long term preservation of meat.

With the introduction of reliable means for refrigeration, i.e., the ability to maintain a low temperature regardless of the external environment, the long-term preservation of raw meat has been greatly enhanced and greatly increased the duration of the preservation. Frequently, in modern meat processing, animals are slaughtered at one place which can be remote from the point of sale and the eventual consumer, and as much as a week can pass before the meat is actually consumed. This lag between the slaughtering of the meat and its consumption requires that the meat be constantly maintained under refrigeration in order

to preserve its quality and prevent its degradation over this time period.

For example, an animal (a cow) may be slaughtered and cut into halves or quarters which are then forwarded to a wholesaler or retailer where they may be divided into smaller cuts such as steaks or roasts. During the transfer of the meat from the slaughter house to the wholesaler or retailer, the meat must be maintained, frequently the meat is frozen in order to preserve its quality. After the meat has been divided into cuts for sale to the eventual consumer, it must also be maintained under constant refrigeration in order to preserve its quality. Under this distribution scheme, it can be from a few days to more than a week before the meat is purchased and consumed. It, therefore, becomes evident that this constant requirement for very low temperatures greatly contributes to the cost of meat.

Another example of the costly disadvantages of very low transportation and storage temperatures can be illustrated by practice of long distance overseas shipment and distribution of frozen meat. Today, freezing is a standard method of distributing meat processed in one region of the world to another region wh r it is to be

consumed. Overseas shipment of frozen meat is both very costly and thawed meat obtained by this method is no longer considered to be "fresh" meat. That is, once a piece of meat has been frozen, by definition it is no longer considered to be "fresh." A method of overseas transportation of meat which maintains the "freshness" of meat transported for distribution would be highly desirable. Since the only method available for long distance overseas distribution of meat is by shipping frozen meat, no method currently exists which would allow for the overseas distribution of "fresh," unfrozen meat.

Transportation of slaughtered meat from the slaughter house to the wholesaler or retailer requires the use of some form of refrigerated transportation, such as refrigerated tractor-trailer trucks. This is a costly mode of transportation since it requires specialized equipment and extra fuel to provide and maintain refrigeration.

In addition to preserving the overall quality and fitness of the meat for consumption, other methods have been derived which are aimed at preserving the color of fresh meat. That is, methods have been developed which maintained for example, the red color of fresh meat, such as beef.

Typical examples of methods for treating raw meat to preserve the color of the meat are disclosed in United States Patent Nos. 3,459,117 to Koch et al., 4,001,446 and 4,089,983 both to Hood, and 4,522,835 and 3,930,040 to Woodruff et al. All of these patents disclose methods or processes for preserving or maintaining the color of meat such as beef, poultry or fish.

Both of the Hood references disclose methods of exposing an animal protein source to a reducing agent and then an environment of carbon monoxide in order to preserve the bright red color of protein source. Additionally, the Hood et al. references only treat slurries of the protein source as this is required for saturation by the carbon monoxide. The source is then mixed with the remainder of the food stuff to prepare a moist dog food. Further, the references are concerned only with the application of carbon monoxide in order to preserve the color of product and both require

subsequent processing, such as canning or heat sterilization, in order to preserve the actual quality and freshness of the product. Additionally, the Hood '983 reference discloses the addition of a sufficient amount of microbiological and bacteriological inhibitors to further preserve the product.

The Woodruff et al. '835 reference discloses a process for maintaining a good color and the freshness meat by first exposing meat to an atmosphere with a small amount of oxygen and then exposing the meat to a modified atmosphere containing a small amount of carbon monoxide to effect the conversion of myoglobin to carboxymyoglobin. A third required step is the maintenance of the meat in an atmosphere of higher than 10% carbon dioxide.

The Woodruff et al. '040 patent discloses a process for storing or shipping fresh meat in a modified gaseous atmosphere. The process requires maintaining refrigerated meat in an artificial atmosphere composed of oxygen, carbon dioxide and carbon monoxide as well as nitrogen. The carbon monoxide may be removed from the modified material after the meat has been treated for at least one hour.

The Woodruff et al. patents teach maintaining the color in meat by treating the meat with a mixture of gases including carbon monoxide. That is, the Woodruff et al. patents teach chemical alteration of the surface of the meat to maintain the color of the meat and utilize refrigeration for meat preservation. Additionally, the Woodruff et al. patents teach the treatment of meat using a gaseous mixture of carbon monoxide, oxygen, carbon dioxide, and nitrogen. This method of treatment results in the creation of a storage environment which has low oxygen concentration and a carbon dioxide concentration of approximately ten percent. This type of gaseous mixture creates optimal growth conditions for the growth of microaerophil bacteria such as *Helicobacter pylori* and *Campylobacter jejuni* which are known to be pathogens which cause widespread gastroenteritis. The Woodruff et al. method of treating meat does maintain the color of fresh meat, however, the Woodruff et al. method has the disadvantage of accelerating bacterial contamination of meat treated by the Woodruff et al. method, thus shortening the storage life of the meat treated thereby.

The Koch et al. '117 patent discloses a cover useful for treating fresh red meat with carbon monoxide in order to maintain the bright red color of the meat. Koch et al., teaches a cover comprised of two films which are sealed together around the edges and which confines a quantity of carbon monoxide gas therebetween. Both film layers are substantially carbon monoxide impermeable when dry, however; when the film is brought into contact with a freshly cut sample of red meat, the moisture in the meat wets the film and transforms the film into a carbon monoxide permeable structure. The carbon monoxide then contacts the meat sample thereby causing the meat to maintain its desired red color.

The Australian Patent Document No. AU-A-18559/92 to Tamayama et al., discloses a method for maintaining and improving the quality of meat by causing meat to contact and absorb carbon monoxide gas in a sealed container and then requiring removal of the carbon monoxide gas from the container. Exemplifying the criticality of the removal of the carbon monoxide gas from the container, the patent requires that the carbon monoxide gas within the container be sucked and discharge by means of a pump.

Heretofore, the treatment of raw meat with carbon monoxide has been taught simply as a mechanism for preserving the color of the meat and, not as a mechanism for the long-term preservation of a meat sample over time in a fresh, non-frozen form.

While the above-disclosed patents teach the exposure of raw meat to gas mixtures containing carbon monoxide or the exposure of meat slurries to carbon monoxide in combination with other steps, they fail to teach a simple method of exposing raw meat solely to carbon monoxide.

In order to overcome the problems and deficiencies of the prior art methods, it is desirable that a method of preserving raw meat be introduced which eliminates the cost and associated problems with the prior art preservation techniques.

Applicant has developed a single step method for preserving meat by exposing raw meat to an atmosphere consisting essentially of carbon monoxide and, then, storing the meat in a sealed container. Unlike prior art preservation methods, no additional steps, compounds or additives are required in order to prevent the growth of microbiological or bacterial organisms.

SUMMARY OF THE INVENTION AND ADVANTAGES

According to the present invention, a method for preserving meat by exposing raw meat to an atmosphere consisting essentially of carbon monoxide is shown. Meat treated according to the present invention may not require any form of subsequent refrigeration under certain conditions and time constraints and can be stored for long periods of time following treatment with the carbon monoxide without significant bacterial growth, without freezing, and without a loss in meat quality.

BRIEF DESCRIPTION OF THE DRAWINGS

Other advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

FIGURE 1 is a bar graph of the relationship between aerobic bacterial growth on a fresh meat sample stored at 22-30°C over time in either a CO treated environment or an air only environment;

FIGURE 2a is a histogram illustrating preservation duration of CO preserved meats and air treated meat preserved at 5 +/- 3°C as determined by Microaerophil growth;

FIGURE 2b is a histogram illustrating preservation duration of CO preserved meats and air treated meat preserved at 5 +/- 3°C as determined by total viable aerobic bacterial growth;

FIGURE 3 is a graph illustrating spectral analysis of the amounts of hemoglobin in the blood of cats that consumed either CO treated meat or air treated meat;

FIGURE 4 is a photograph illustrating meats, the colors of meat treated with (A) vacuum only, (B) N_2, (C) air, and (D) CO;

FIGURE 5 is a photograph illustrating the color change in meat treated without CO (left) and meat treated with CO (right);

FIGURE 6 is a photograph illustrating the internal color change of meat treated without CO (left) and meat treated with CO (right);

FIGURE 7 is a photograph illustrating the color change of a piece of fresh CO treated meat stored at 5°C for three days;

FIGURE 8 is a photograph illustrating the same meat sample shown in Figure 7 stored with CO at 5°C for ten days;

FIGURE 9 is a photograph illustrating a transverse cut of the meat sample shown in FIGURE 8 made at 7 cm from the edge showing homogenous bright red color;

FIGURE 10 is a photograph illustrating transverse cuts of CO treated (left) and frozen (right) meat samples after twelve days of storage;

FIGURE 11 is a photograph of the transverse cuts of meat shown in FIGURE 10 after cooking;

FIGURE 12 is a photograph illustrating transverse cuts of the cooked meat samples shown in FIGURE 11; and

FIGURE 13 is a photograph illustrating a section of CO treated meat as shown in FIGURE 10, following exposure to open air at 5°C for two weeks, at the end of this two week period, the meat sample was ground, a 200 gram "hamburger-like" sample was cooked and released CO was measured, (top) prior to cooking, (bottom) following cooking.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Generally, the present invention provides a method for preserving meat by exposing raw meat, processed or not, to an atmosphere consisting essentially of carbon monoxide (CO) and, subsequently, storing the meat in a sealed container.

For the purposes of the present invention, the term "meat" is defined to include all types of fresh meat and fresh poultry such as beef, pork, veal, lamb, chicken, turkey, fish and the like. The meat may be in the form of carcasses, primals (e.g., quarters), subprimals (e.g., top round), or retail cuts (e.g., steaks, ground meat and roasts). The process is also effective on whole animals including, but not limited to, cattle, chickens, and fish. Unlike prior art methods, the meat need not be slurried or

otherwise pretreated. "Fresh meat" is defined as a meat article which has not been frozen and subsequently thawed before its sale or consumption.

By preserving, it is meant that the meat maintains a pleasing color, does not spoil and develop a foul smell, bacterial growth is significantly inhibited or retarded, and remains completely pleasing, edible and consumable by humans and other animals. Preservation is not only maintained on the surface of the meat, but also throughout the entirety of the meat. That is, the meat is preserved throughout the thickness of the meat. "Pleasing color" implies that the color of the meat, preserved by the method according to the present invention, is such that it stimulates the appetite to consume the meat. That is, the color and odor of the preserved meat is such that a consumer would be enticed by the meat and would want to consume the meat. Again, meat color is also preserved throughout the thickness of the meat.

The term "without freezing" is defined as storing the meat wherein the temperature is kept between approximately -2 to 30°C. The term "without freezing" also excludes the use of any device or method for freezing the meat. Such

devices include, mechanical or electrical refrigeration devices such as refrigerators, freezers, coolers, and chillers. This term also excludes the preservation of meat by freezing through storage on ice.

Exposing raw meat to an atmosphere consisting essentially of carbon monoxide is defined as bringing into intimate contact both carbon monoxide gas and the meat being treated. The atmosphere preferably consists of carbon monoxide. This term also includes the complete conversion of myoglobin present in the meat sample to carboxymyoglobin and, the complete conversion of myoglobin to carboxymyoglobin/carboxyhemoglobin in fish. The meat is completely immersed or saturated with carbon monoxide.

More specifically, a cross-section of meat is completely immersed in or saturated to its core with carbon monoxide from the exposed surfaces through the entire cross-section (thickness) including its core region and retains the carbon monoxide until the meat is cooked. Thus, as stated above, the meat is preserved throughout its thickness.

Carbon monoxide is inherently a very inert gas. Carbon monoxide is relatively more inert than nitric oxide gas (NO) released from nitrites which have been used as preservatives for meat for several hundred years. Carbon monoxide is a normal metabolite in the body. It is produced indigenously as a product of heme catabolism (mostly the breakdown of hemoglobin). Carbon monoxide is further converted to carbon dioxide and is released from the body in that form. Recently, it has been found that normal metabolism utilizes carbon monoxide as a neurological messenger. (Baranaga, 1993) The high toxicity of carbon monoxide generally stems from its ability to compete with oxygen for binding to hemoglobin.

Practically all of the carbon monoxide (over 99.9%) taken up by meat will be maintained as hemoglobin and myoglobin (Hb/Mb) bound forms. The distribution of carbon monoxide in the meat is assumed to be about half in each globin type. This estimation is based on the fact that mammalian muscles contain approximately two-thirds of their globins as hemoglobin and one-third as myoglobin, but when muscle becomes packed as meat, it looses a portion of its hemoglobin.

Both hemoglobin and myoglobin bind carbon monoxide much more strongly than oxygen. Native Hb/Mb contain iron and divalent oxidation state (Fe^{+2}) and only in this form are Hb/Mb capable of binding the gas ligands O_2, NO, and CO. Following any change in the iron oxidation state, Hb/Mb loose their CO binding ability. Denaturation of the proteins (e.g. by heat) can also result in loss of CO binding potential (as well as other ligands).

Hb/Mb are established catalyzers of the oxidation process in biological tissues. Under regular atmospheric conditions, the Hb/Mb in fresh meat, which are in their native form, exist in a O_2 bound form, the so-called oxy-Hb/Mb. Oxy-Hb/Mb tends to undergo autooxidation to met-Hb/Mb namely the oxidation of the Hb/Mb divalent iron to Fe^{+3} can concomitantly with the formation of superoxide anion O_2^- by the reaction

$$\text{oxy-Hb/Mb } (Fe^{+2}...O_2) \rightarrow \text{Met Hb}(Fe^{+3}) + O_2^-$$

The superoxide anion is unstable and further forms hydrogen peroxide (H_2O_2) which together with Hb/Mb acts as a highly active peroxidation system. Met-Hb/Mb no longer binds any of the gas ligands including carbon monoxide. On the other hand, the Met-Hb/Mb are catalyzers of

oxidations. Unlike the case of oxygen bound to Hb/Mb, in a carbon monoxide bound form, Hb/Mb are protected from autooxidation. Therefore, to protect meats from autooxidation, carbon monoxide is best applied to fresh meat.

It is thought that the mechanism for carbon monoxide preserving of meat is the much greater affinity of myoglobin for carbon monoxide than for oxygen. Following this mechanism, carbon monoxide out-competes oxygen for binding onto myoglobin molecules within the meat structure. By completely displacing oxygen, the micro-environment of the meat becomes more anaerobic and, thereby, prevents or inhibits the growth of aerobic microorganisms, such as *Escherichia coli*, which are responsible for spoilage and degradation of fresh meat and illness. Anaerobic bacterial growth, such as *Microaerophils*, is also inhibited when this method is utilized. This proposed mechanism of carbon monoxide action is merely for illustrative purposes and in no way should be construed as limiting.

The ability to inhibit or prevent the growth of microorganisms allows for the extended storage of meat treated according to the present method. That is, meats treated according to the present invention have a longer storage life and remain both viable and edible in a non-contaminated form for periods longer than those available using current preservation techniques.

In the practice of the present invention, meat samples are placed in an enclosure or container and flushed or exposed to carbon monoxide gas.

The process consists of two stages:

(A) "Meat packing" which refers to introducing the meat into a confined CO atmosphere. "Packed meat" refers to meat which has undergone the meat packing part of the process.

(B) "Meat preservation" which involves maintaining the "packed meat" until it reaches the consumer.

Meat Packing

The container for treatment, storage, and transportation of meat by the method of the present invention can be constructed of various gas-impermeable material such as plastic, metal, and

other materials known in the art. The container can be equipped with both gas inlet and outlet channels which can be opened to allow the influx of gas (CO) or closed in order to render the container sealed.

A suitable container would be capable of maintaining a seal to prevent the escape of carbon monoxide gas from the container. For example, the container can be a sealed room in which large amounts of meat may be treated at a given time, the container can also be a smaller sealable container or chamber. Preferably, the container is of larger volume than the volume of meat being treated to allow for a greater volume of carbon monoxide gas to contact the meat sample.

In a preferred embodiment of the invention, meat samples are treated and stored within plastic bags constructed of a material which is safe for the storage of food products such as polyvinylidene chloride. Preferably, the plastic bags will be constructed of a material that is impermeable to the passage of gases therethrough. Thusly, the meat is maintained in the carbon monoxide atmosphere within the bag (container) during storage.

After a piece of meat to be treated according to the method of the present invention is placed in a suitable container, the container is then filled with the CO gas. The addition of the CO gas can be accomplished in any suitable manner; however, the preferred methods include first removing the gas atmosphere present in the container (usually air) by using a vacuum pump, as is well known in the art, to remove any gases present and the container. The container is then filled with CO from a source such as a gas cylinder.

The container is connected to the CO containing cylinder and CO is introduced. Input and output pressures are measured during the filling process. The input pressure is generally maintained within a range of approximately 1.5 to 5.0 atmospheres. The preferred pressure is approximately 2.0 atmospheres. Upon reaching the preferred pressure in the output, the gas flow is stopped and excess gas is allowed to escape until the pressure within the container reaches approximately 1.0 to 1.2 atmospheres. The preferred gas pressure in the container is approximately 1.1 atmospheres.

During the gas filling operation, the ambient temperature of the surrounding can be maintained between -2 to 37°C.

The parameters that govern gas filling or exposure time vary depending on the pressure of the gas input, the dimensions of the inlet and outlet channels, and the dimensions of the container.

For meat packing, exposure of only the surfaces of the meat to carbon monoxide is generally required. However, for the purposes of meat preservation, the gas filling time should be long enough to allow for a sufficient amount of CO gas to be completely absorbed (throughout its thickness) into the meat undergoing treatment. That is, enough CO gas is flushed through the container to allow for the complete penetration and protection of the meat being treated.

The gas filling time generally ranges from approximately one to thirty minutes with the preferred filling time being approximately five minutes. For the purposes of this invention, exposure time is defined as the gas filling time. Again, it should be noted that the length of exposure of the carbon monoxide to a meat sample will vary depending on the size of the meat sample and the weight of the meat sample being treated.

That is, a larger and heavier meat sample will require a longer period of exposure to the carbon monoxide in order to achieve long-term preservation. In other words, a larger meat sample will require a longer exposure to carbon monoxide in order to properly preserve the meat sample without the freezing.

The temperature during the carbon monoxide exposure is preferably between -2 and 37°C and can vary depending on the temperature selected to in order to carry out the method.

Meat treated as previously described above generally contains from 5 to 100% by weight or volume of CO gas. The preferred volume of CO in the treated meat is approximately 30% of the weight of the meat (e.g. 30 ml for 100 grams of treated meat).

Under the meat preservation method of the present invention, the meat surface is initially contacted with the CO gas. Since the surface of the meat is the most prominent site for the presence of bacteria, the meat treated by the method of the present invention is immediately protected. Further, while sealed in the container, penetration of the CO gas continues until the entire meat mass has been penetrated and, thereby,

protected. This total penetration allows for the complete substitution of both hemoglobin and myoglobin by the carboxy forms of these compounds as is shown in the following examples. The total CO treatment of the meat throughout its thickness also enables meat which has been treated according to the present invention to maintain a pleasing color for extended periods of time after the meat has been removed from the packaging or container in which it was treated. That is, as shown in the following examples, meat treated according to the present invention can be transported, unpacked, and then maintained in a fresh form for a further extended period of time without a loss of color or quality.

The above discussion provides a factual basis for the use of the present invention as a method of long-term preservation of meat at different temperatures without freezing. The examples also demonstrate the preservation of the meat after undergoing the treatment of the present invention. The methods used with and the utility of the present invention can be shown by the following examples.

EXAMPLES

Example 1.

The Effect of CO Exposure On Time Dependent Changes in Meat Color:

Samples of fresh meat (30 grams of beef, veal, or turkey) treated with CO by the method of the present invention were incubated in a suitable container for thirty minutes at a temperature of 15±3°C. Control samples were treated identically to CO-treated meats but were treated with air. The meat samples were removed from the container and were placed on an open benchtop at 15±3°C, or in an air exposed thermostatically controlled environment at 37°C. The color of the air treated meats turned brown gradually (within three hours at 37°C and twelve hours at 15±3°C), indicating non-fresh or spoiled meat. In contrast, the CO-treated meat samples maintained a wine-red color for at least 24 hours following exposure.

Example 2.

Comparison of CO, air, N_2 and vacuum treated meats

Fresh meat quarters (beef) were kept for six days at -2°C. The meat was then cut into 30 gram pieces (4" X 2" X 0.1") and divided into four groups and treated as follows: (A) vacuumed and (2-4) were introduced into gas tight containers by method previously described above and filled at a pressure of 1.1 atmospheres with gas at a volume which was ten time (10X) the volume of the meat. The gases used were: group D filled with CO, group B filled with N_2, and group C filled with air. A portion of the samples was kept at 15±3°C and the rest at 7°C. After twenty-four hours at 15±3°C and 48 hours at 7°C time dependent changes in color were observed. The samples of group A (maintained solely under vacuum) were brownish-purple. The samples of group B (N_2 treated samples) were brownish-red. The samples of group C (air treated samples) were brown. However, the color of the samples of Group D (CO treated) were unchanged remaining bright wine-red as shown in Figure 4.

Example 3.

Color Changes in Large Meat Chunks:
Time Dependency During Meat Preservation

Beef chunks of 0.5 - 1.5 Kg were turned into CO-treated meat samples by treating with a 100% meat volume of gas according to the method of the present invention. Control chunks from the same source were treated identically but with air instead of CO. All of the chunks were kept at 4°C. The surface color of the air treated meat became brown after three days. The meat chunks were cut transversely for observation of color changes. Color change propagated with time in all meats from the surface towards the center of the chunk and were brown in air treated samples and wine-red in CO-treated samples. Following eighteen days of incubation, the air treated chunks were completely dark brown. In the CO-treated meat, the color change was 3-5mm from the surface after one and a half hours. Twelve hours post treatment a two cm ring of color change was observed. Three days post treatment, only five percent of the area of the transverse section remained unchanged. After seven days post treatment the color change was complete.

Propagation of the color from the surface into the interior of the chunks for chunks kept under 5% meat volume of gas was somewhat slower as compared to those chunks maintained kept under 100% meat volume gas. It is important to note that care should be taken to prevent adherence of any of the meat surface to the container.

Example 4.

Color Changes in Large Meat Chunks; Time Dependency After Removal From Container

An experiment similar to the previous example was performed except that the CO-treated meat chunks and the air treated meat chunks were removed from their containers after 21 days. The colors observed were the same as in the previous example. The chunks were left open to the atmosphere at 4°C. The color of the CO-treated was maintained for fourteen days. At day 14, only the surface (<1mm deep) of the CO-treated meat was brown. The color of the air treated meat remained dark brown throughout as shown in Figures 5 and 6.

Example 5.

Comparison of Bacterial Growth Under Air, CO and N_2 Atmospheres

Meat samples weighing 4.00±0.18 grams, were treated by flushing with either air, CO, or N_2. After twenty-four hours of storage at room temperature (15±3°C) each of the treated meat samples was soaked in sterile 0.15M sodium chloride (1ml per 2 grams of treated meat) for ninety minutes to extract any bacteria present on the surface of individual samples. Aliquots of serial dilutions of the extracts were plated onto non-selective agar plates (Bactoagar, Difco) and on Gram negative selective plates (MacConkey, Difco). All the plates were incubated over night at 37°C to allow bacterial growth. Bacterial colony counts per gram of meat (mean ± SD) are summarized in Table 1.

TABLE 1

Gas in Atmosphere	No. of colonies grown on bactoagar	gram negative
Air	$(1.42\pm0.3)X10^6$	$(2.74\pm1.12)X10^6$
N_2	$(1.63\pm0.3)X10^6$	$(0.46\pm0.25)X10^6$
CO	$(0.29\pm0.01)X10^6$	$(0.02\pm0.01)X10^6$

Example 6.

Toxicity and Edibility of CO-Treated Meat

Samples of CO treated meat of approximately 30 grams in weight or ground meat samples were stored for up to seven days at a temperature between 4 to 10°C. Samples of the CO treated meat were given to twelve starved cats (4kg per cat). Under these conditions, the meat samples were immediately consumed. No mal-effects were observed in any of the animals within 48 hours post consumption.

Additionally, four dogs each of which weighing approximately fifteen kilograms was offered 100 to 150 gram sample of CO preserved meat. The samples were consumed by the dogs and no mal-effects were observed in any dog within 48 hours after consumption.

Cats were fed fresh CO treated meat (250 grams per day per cat for one week). A control group was fed meat from the same source which was treated identically but with air instead of CO. The animals were continuously monitored by animal-tenders and showed regular behavior. The animals were found healthy by a house veterinarian. At the end of the experiment, a blood sample was drawn from all the animals and the red blood cells

were separated. The state of hemoglobin in these cells was analyzed spectrophotometrically as shown in Figure 3. From the spectra, it was found that the hemoglobin of both groups was completely in the oxy-hemoglobin form indicating no CO in the blood of the animals fed CO-treated meat.

Example 7.

Determination of Shelf-Life Extension by Bacterial Count as Limited by International Control Standards: Preservation at Room Temperatures.

General Methods:

Meat packing: Freshly slaughtered meat (beef) chunks of 0.5-1.5 Kg were cut into 25cm^2 pieces, 0.5-1.0 cm width (12-20 grams). Four samples were immediately submitted to bacterial count (as described below). The rest of the samples were treated with CO according to the method of the present invention. The gas pressure was 1.1 atmospheres and the volume of gas was equal to (100%) of the meat weight. The gas content was either air or 100% CO. The samples were preserved within a predetermined temperature range. Bacterial growth was measured at time intervals determined according to the temperature of preservation.

Evaluation Of Hemoglobin And Myoglobin Oxidation State In CO Treated Meats:

The quality of the CO-treated meats depends on the amount of globin fractions converted to CO bound forms and their location. The location is important since bacterial growth starts on the surface of the CO-treated meats as does CO penetration. Assessment of the CO bound myoglobin and hemoglobin in the CO-treated meats was carried out using two parameters: (a) measurements of the circumference width of zones which underwent visible color change due to CO binding (CO-treated meats were successively cut transversely and the depth of the color-changed zone was measured with a ruler) and (b) assessment of the CO bound fraction of hemoglobin and myoglobin in CO-treated samples.

Procedure: Samples of the CO-treated meats (1 to 5 grams) were homogenized in an equal volume of phosphate buffer (0.1M, pH 7.4) to extract both hemoglobin and myoglobin. The extract was centrifuged at 40,000 g for ten minutes. The supernatant was isolated and its absorption spectrum was measured in the 400 to 700nm range. From the position of the absorption peaks and their relative heights the fraction of CO bound globins was calculated.

Bacterial growth measurement was made according to international standards and carried out by a ISO 9000/IEC Guide 25 licensed bacteriological laboratory. As bacterial growth is mostly on the meat surface, the routine contamination tests at governmental laboratories relate to bacterial growth on a standard minimal area of $25cm^2$. The bacterial growth is then expressed as the number of bacteria per cm^2. The most stringent standards allow a growth of up to $5X10^6$ (6.7 in log scale) bacteria per cm^2 while the least strict ones consider a growth of up to $1X10^7$ (7.0 in log scale) non-contaminated.

The procedure entails treating a 25 cm^2 surface area sample of the meat with 25 ml of aqueous solution. The bacterial content is introduced into the solution using a stomacher apparatus (Seward Lab U.K.). This suspension is then diluted in a ten fold series up to 10^{-9} in 0.1 M phosphate buffer, pH 7.0. One ml of each dilution is applied to each of three types of 60mm growing plates: (a) containing plate count agar (PCA, Difco) incubated at 33°C±0.2 for 48 hours to enable total viable aerobic count, (b) containing SPS agar (Difco) allowing clostridium growth, and (c) containing the same medium as a (a) allowing

microaerophile growth. Type (b) and (c) plates were confined within sealed anaerobic jars supplied with gas generating kits (Oxoid, U.K.) and incubated for twenty four hours at 35°C. Bacterial colonies (up to 200 per plate) were counted using a colony counter.

According to international health standards, the maximal bacterial growth allowed for non-contaminated meat is $1X10^7/cm^2$ total viable aerobic bacteria and $1X10^4/cm^2$ of microaerophils. The shelf life of a meat in a non-contaminated form was determined by the duration until the above defined bacteria levels were reached ("preservation duration").

Twenty experiments were carried out as follows: meats samples were preserved at 5±3.5°C and bacterial counts were carried out at intervals of four days. The length of "preservation duration" in these experiments (expressed as mean ±SE) were for microaerophils: 8.72±2.1 days for air treated samples and 18.9±3.27 for CO-treated samples (see Figure 2a); by the criteria of total viable aerobic bacteria 11.13±1.11 days for air treated meat samples and 23.12±2.79 for CO-treated meat samples (see Figure 2b).

This data shows that the meat preservation method of the present invention succeeded in extending the shelf life more than two fold.

Example 8.

Determination of Meat Shelf-life Extension by Bacterial Count as Limited by International Control Standards: Preservation at High Room Temperature

As in the previous example, meat samples were preserved at 26±4°C. Due to the high temperature which accelerates bacterial growth, bacterial count was determined at five hour intervals. Four experiments were carried out and the length of "preservation duration" in these experiments (expressed as mean ±SE) were: by the criteria of total viable aerobic bacteria 13±1 hours for air treated samples and 30±1 hours for CO-treated samples (see Figure 1). By the microaerophils count criteria: 9.5±0.9 hours for air treated samples and 9.5±0.8 hours for CO-treated samples.

Example 9.

Inhibition Of Bad Odor
Development In CO Treated Meats

In all meats preserved as in examples 1 through 8, it was found that by the time of detection of bad odors in air preserved meats, no similar odor was detected in the CO-treated meats. This finding indicates that the arrest of meat-spoilage was achieved by the meat preservation method of the present invention. Consistently, in all preserved meat samples bad odor was detectable in samples which showed high count of bacteria. Additionally, by the time bad odor was detectable by the average human nose, the total viable aerobic count exceeded 10^8 colonies/cm^2, a value which exceeds that allowed for non-contaminated meats (10^7 colonies/cm^2). Thus, odor is a less sensitive indicator of meat spoilage than bacterial count. However, odor is valuable because it can be used by most people including the meat consumers.

Table 2 represents the "preservation duration" under various conditions at which CO-treated meat retained pleasing odors while air preserved meat smelled badly.

TABLE 2

Type of meat	Size	Temperature range of preservation, °C	"Preservation duration in days
Beef	Slices	2-9	18
		22-30	3
Beef	Chunks	2-9	18
	Chunks	14-17	7
Veal	Slices	22-30	3
Turkey	Slices	22-30	3

Example 10.

CO Diffusion From Meat Surface into the Core During the Preservation

Meat samples were sealed in plastic bags under 100% CO at a pressure of about 1.1 atmosphere. CO volume was 30 ± 20% of the meat volume. The bags were kept at 5°C. Figures 7-9 demonstrate a typical experiment in which meat was treated 24 hours after slaughter. A sample of calf meat weighing 18 pounds (about 8 Kg) was cut into two nine pound pieces having maximum length of 30 cm and maximum width of 20 cm. One of these samples

was kept frozen at -18°C while the other was preserved in CO at 5°C. After three days, the bag was opened to release the unbound CO and the meat was left in the open air for half an hour. The meat sample was cut transversally at about one third of its length (7 cm from one edge). About 30% of the meat radius (from surface to core) changed in color from dark to bright red (see Figure 7). Because any CO which reaches Hb/Mb bind quickly, the change in meat color serves as a measure of the CO diffusion rate.

The meat samples were reassembled and repacked with CO. Following seven additional days at 5°C, the meat samples was again unpacked and cut transversally once in the middle of the sample, about 15cm from the edge (shown in Figure 8), and once closer to the end of the sample, at about one third of the sample's length (shown in Figure 9). As shown in the transverse cut in Figure 8, the meat was almost completely bright red except for a small dark red area shown by an arrow. This indicates a nearly complete diffusion or saturation of the CO from the surface to the core of the meat sample. The cut at one third of the sample's length shows that in this zone, oxy-Hb/Mb were completely converted to their carbomonoxy forms as

shown in Figure 9. The meat samples were reassembled and kept at 5°C under CO for an additional two days to ensure complete conversion of Hb/Mb to the carbomonoxy forms. After 12 days under CO at 5°C, the color of a middle sample (transverse cut) differed dramatically from that of the frozen sample (see Figure 10), indicating that oxy-forms of Hb/Mb were preserved in the frozen meat sample (Figure 9, right) while carbomonoxy forms prevailed in the CO treated meat (Figure 10, left).

Example 11.

Appearance of the Cooked Meats

From the 12 day-old, frozen and CO treated meats (shown in Figure 10), 5cm in width pieces were cut transversally. Each piece was cooked in 100 ml distilled water in a covered pot on a low flame for 120 minutes. At the end of the cooking period, all of the water had evaporated. The appearance of the cooked meat pieces is shown in Figure 11. They were similar except for some browning of the surface of the CO treated meat due to complete water loss in the meat.

To reveal the meat interior, the two pieces were cut transversally. A small test by ten different people assured that pieces smelled alike having a typical cooked meat smell. The transverse sections are seen in Figure 12 and were very similar in appearance. This experiment demonstrates the loss of the bound CO during the cooking process (heating) which leads to protein denaturation and heme degradation.

Example 12.

Measurements of CO Release in the Process of Cooking

A. Experimental procedure:

All measurements of CO release in the process of cooking were carried out in a 7.5 liter sealed regular pressure pot ("pressure cooker") to which manometer/thermometer was inserted to measure the temperature and pressure during cooking. The pot was also equipped with a controlled outlet (valve). To ensure complete sealing the pot lid was also smeared with a layer of high vacuum grease prior to locking the pot. The pot was then heated by cooking gas for a few minutes until reaching a pressure of 1.5 atmospheres and a temperature of 235°F (113°C). At this stage the pot was transferred to an electric heater for further

cooking keeping the pressure within the pot at 1.7±0.7 atmospheres and the temperature at 114± 12°C. Cooking time varied among experiments within the time range of regular domestic cooking, namely 60-140 minutes. The pot was allowed to cool until reaching room temperature and then was connected via the valve to a CO monitor. The CO level in the pot atmosphere was expressed in PPM.

The measure CO level in PPB(m) was translated and expressed as CO PPM(c) released from 2 Kg of cooked meat (a family meal size) into a sealed room of 3.0 square meters (kitchen size dimensions). Considering the volume of one mole of gas at room temperature as 22.4 liters, the expected CO level was calculated as:

$$PPM(c) = 0.074 \cdot PPM(m)/X$$

Where: PPM(c) = calculated PPM;

PPM(m) = measured PPM;

X = meat weight in grams.

B. Safety in cooking the CO treated meat:

200-650 gram meat samples (either in one piece or ground) were treated with CO and stored within a confined CO atmosphere for 14 days at 5°C. The meats were cooked within 30 minutes of removal from the CO packaging bags. The results (expressed

as explained above) are summarized in Table 3. As can be seen, the average PPM(c) level given as Mean ± S.D. (N) was 0.056 ± 0.026 (10). In all experiments, less than 0.1 PPM of CO was released from 2 Kg cooked meat into the hermetically closed room. Since the TLV for CO is 25 PPM, it can be seen that the released CO level from the cooked meat (2Kg) in our experiments, was far below that safety limit. In fact it is low enough not to alarm a domestic CO detector (100 PPM for 90 minutes in a regular room size). Thus, under our experimental conditions, the consumer is not exposed to danger. Moreover, treated meats could be removed from their CO packing bags and maintained for at least 14 days in the open air at 5°C without any risk of CO release prior to cooking.

No statistically significant test analysis could be made because the experimental conditions were incomparable (chosen to cover various cooking conditions). However, there is a trend showing that the level of released CO is inversely correlated with the post-slaughter period until CO treatment began. Thus, the sooner (closer to slaughtering) the meat was treated, the higher the CO level (see the declining order in items 1-4

in ground meat in Table 3). Note that CO release level reflects the CO bound level in the meat. These findings agree with a slow autooxidation of Hb/Mb in meats exposed to air prior to CO packing, resulting in formation of met-Hb/Mb which can no longer bind CO. Therefore, upon packing, less CO will be bound and consequently less CO will be released later upon cooking. The data from the experiments (items 6-8a in Table 3) suggest that up to a period of two days post-slaughter, CO release level was similar.

From items 8a-8c (Table 1), wherein the portions of the same CO treated sample were removed from the CO packing bag and exposed to open air for various periods, it appears that the CO was maintained within the samples for at least three days.

Example 13.

Release of CO by Cooking

Freshly drawn human blood was used. The red cells were washed and lysed in a hypotonic buffer. The mixture was centrifuged to separate cytosol from membranes. The concentration of hemoglobin in the solution was measured spectrophotometrically and was found to be 16.2 mM.

The solution was sealed in a beaker and CO was gently flushed above the solution surface while stirring for 30 minutes. A few grains of dithionite was added to consume any residual oxygen. The color of the solution turned bright red typical of carbomonoxy Hb. The solution was then left while stirring (for 15 minutes) to the open air to released dissolved CO. The Hb was identified spectrophotometrically as carbomonoxy Hb. The hemoglobin solution was cooked exactly as the meat and the amount of CO in the pot atmosphere was measured. From the concentration of hemoglobin (each heme molecule binds one CO molecule) the amount of CO molecules was calculated in the solution. From this amount and the pot volume, the expected PPM level of totally dissociated CO was calculated. As in the procedure of cooked meats the gas level in the pot was measured by the CO monitor. The ratio of measured to calculated CO level turned out to be 1.06 indicating that, within experimental error, all CO was indeed released from the Hb by cooking.

TABLE 3: CO RELEASE FROM COOKED MEATS

Item No	Meat form	Post Slaughter period to treatment (days	PPM(c) of CO
1)	Ground	6	0.052
2)	Ground	8	0.039
3)	Ground	8	0.039
4)	Ground	10	0.013
5)	Ground	1(14)*	0.033
6)	Chunk	0	0.093
7)	Chunk	0	0.053
8a)	Chunk	2	0.071
8b)	Chunk	2(1)*	0.076
8c)	Chunk	2(2)*	0.088

All meats (200-650 gr) were treated with CO and were stored in CO atmosphere for 14 days at 5°C. The meats were cooked within 30 minutes after exposure to air. (*) refers to exposure period at 5°C (in days) in the open air following removal from CO packaging bags. Items 8a-c are sub-chunks which were left in th open air for different time periods. Average PPM(c) = 0.056 ± 0.026

The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

REFERENCES CITED

Baranaga, "Carbon Monoxide: Killer to Brain Messenger in one Step", Science, 259, 309 (1993).

CLAIMS

What is claimed is:

1. A method for preserving meat by:
exposing raw meat to an atmosphere consisting essentially of carbon monoxide and maintaining the meat in a vacuum free, sealed container to maintain color and freshness while retarding bacterial growth.

2. A method as set forth in claim 1 wherein said exposing step is further defined as completely immersing the meat throughout with an atmosphere consisting essentially of carbon monoxide.

3. A method as set forth in claim 1 wherein said exposing step is further defined as exposing the meat to carbon monoxide gas for approximately 1 to 30 minutes prior to sealing the container.

4. A method as set forth in claim 3 wherein said exposing step is further defined as exposing the meat to carbon monoxide gas for approximately five minutes prior to sealing the container.

5. A method as set forth in claim 1 wherein said exposing step is further defined by exposing the meat to a volume of carbon monoxide ranging from approximately 5 to 100 percent by weight or volume of meat being treated.

6. A method as set forth in claim 5 wherein said exposing step is further defined by exposing the meat to a volume of carbon monoxide of approximately thirty percent by weight or volume of meat being treated.

7. A method as set forth in claim 1 wherein said exposing step is further defined as exposing the meat to carbon monoxide gas between a temperature range of approximately -2 to 37°C.

8. A method as set forth in claim 1 wherein the sealed container is a plastic bag.

9. A method as set forth in claim 1 wherein the sealed container is a sealed chamber.

10. A method as set forth in claim 1 wherein the carbon monoxide in the container has an atmospheric pressure of approximately 1.5 to 5 atmospheres.

11. A method as set forth in claim 10 wherein the carbon monoxide in the container has an atmospheric pressure of approximately 2.0 atmospheres.

12. A method as set forth in claim 1 further including the step of storing the meat at a temperature above freezing following said carbon monoxide exposure step.

13. A method as set forth in claim 12 wherein the temperature is further defined as a temperature range from approximately -2 to 30 °C.

14. Meat treated and preserved by the process comprising the steps of:

exposing raw meat to an atmosphere consisting essentially of carbon monoxide and maintaining the meat in a vacuum free sealed container to maintain color and freshness while r tarding bacterial growth.

15. Meat treated and preserved by the process according to claim 14 wherein said exposing step is further defined as completely immersing the meat throughout with an atmosphere consisting essentially of carbon monoxide.

16. Meat treated and preserved by the process according to claim 14 wherein the exposing step is further defined as exposing the meat to carbon monoxide gas for approximately one to thirty minutes prior to sealing the container.

17. Meat treated and preserved by the process according to claim 14 wherein the exposing step is further defined by exposing the meat to a volume of carbon monoxide for approximately five minutes prior to sealing the container.

18. Meat treated and preserved by the process according to claim 14 wherein the exposing step is further defined as exposing meat to a volume of carbon monoxide ranging from approximately 5 to 100 percent by weight or volume of meat being treated.

19. Meat treated and preserved by the process according to claim 14 wherein the exposing step is further defined as exposing meat to a volume of carbon monoxide of approximately 30 percent by weight or volume of meat being treated.

20. Meat treated and preserved by the process according to claim 14 wherein the sealed container is a plastic bag.

21. Meat treated and preserved by the process according to claim 14 wherein the sealed container is a sealed chamber.

22. Meat treated and preserved by the process according to claim 14 wherein the carbon monoxide in the container has an atmospheric pressure of approximately 1.5 to 5 atmospheres.

23. Meat treated and preserved by the process according to claim 21 wherein the carbon monoxide in the container has an atmospheric pressure of approximately 2.0 atmospheres.

24. Meat treated and preserved by the process according to claim 14 further including the step of storing the meat at a temperature above freezing following the carbon monoxide exposure step.

25. Meat treated and preserved by the process according to claim 14 wherein the temperature is further defined as a temperature range from approximately -2 to 30 °C.

26. Meat treated and preserved by the process according to claim 14 wherein said exposing step is further defined as exposing the meat to carbon monoxide gas between a temperature range of approximately -2 to 37°C.

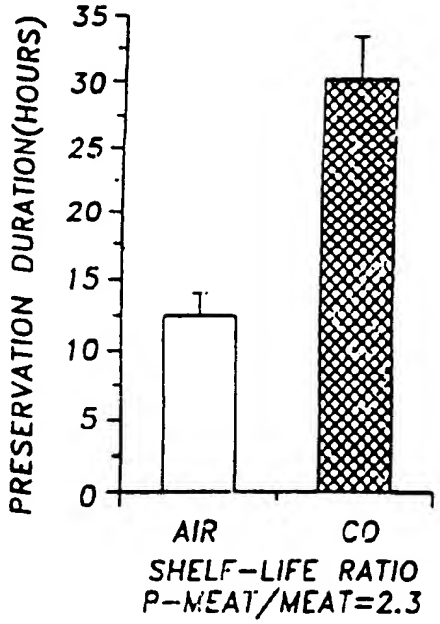


Fig - 1

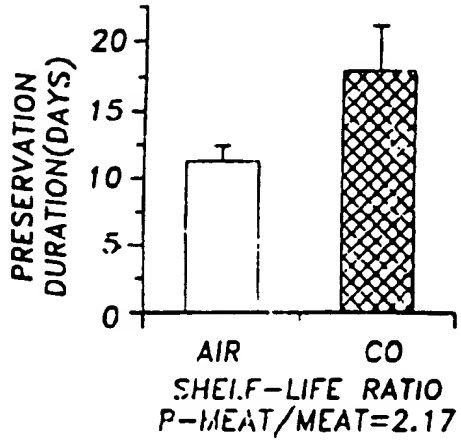


Fig - 2a

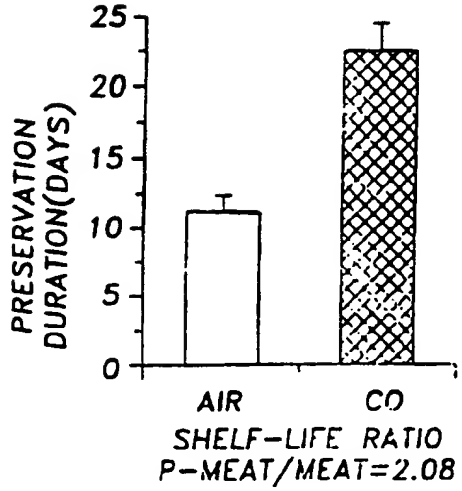


Fig - 2b

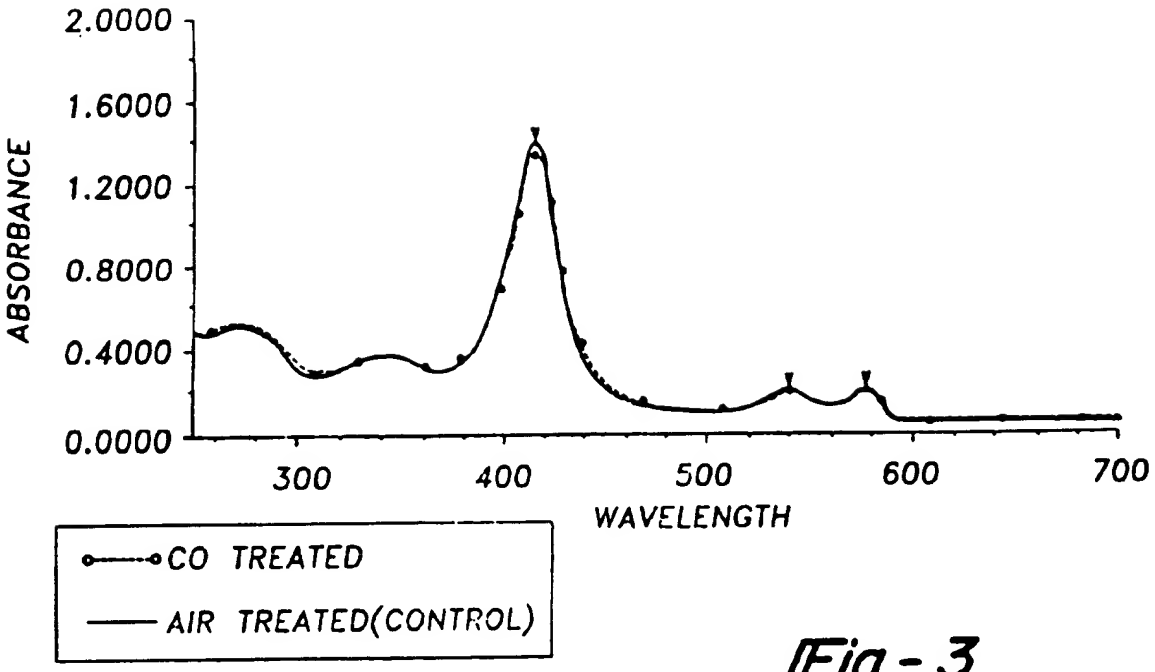

2.0000
1.6000
1.2000
0.8000
0.4000
0.0000
ABSORBANCE
300
400
500
600
700
WAVELENGTH
CO TREATED
AIR TREATED(CONTROL)

Fig - 3

BEEF STEAKS MAINTAINED
IN SEALED PLASTIC BAGS FOR 24 HOURS

A. VACUUM PACKED (7°C)
B. FILLED WITH NITROGEN (15±3°C)
C. FILLED WITH AIR (15±3°C)
D. FILLED WITH CO (15±3°C)

Fig - 4

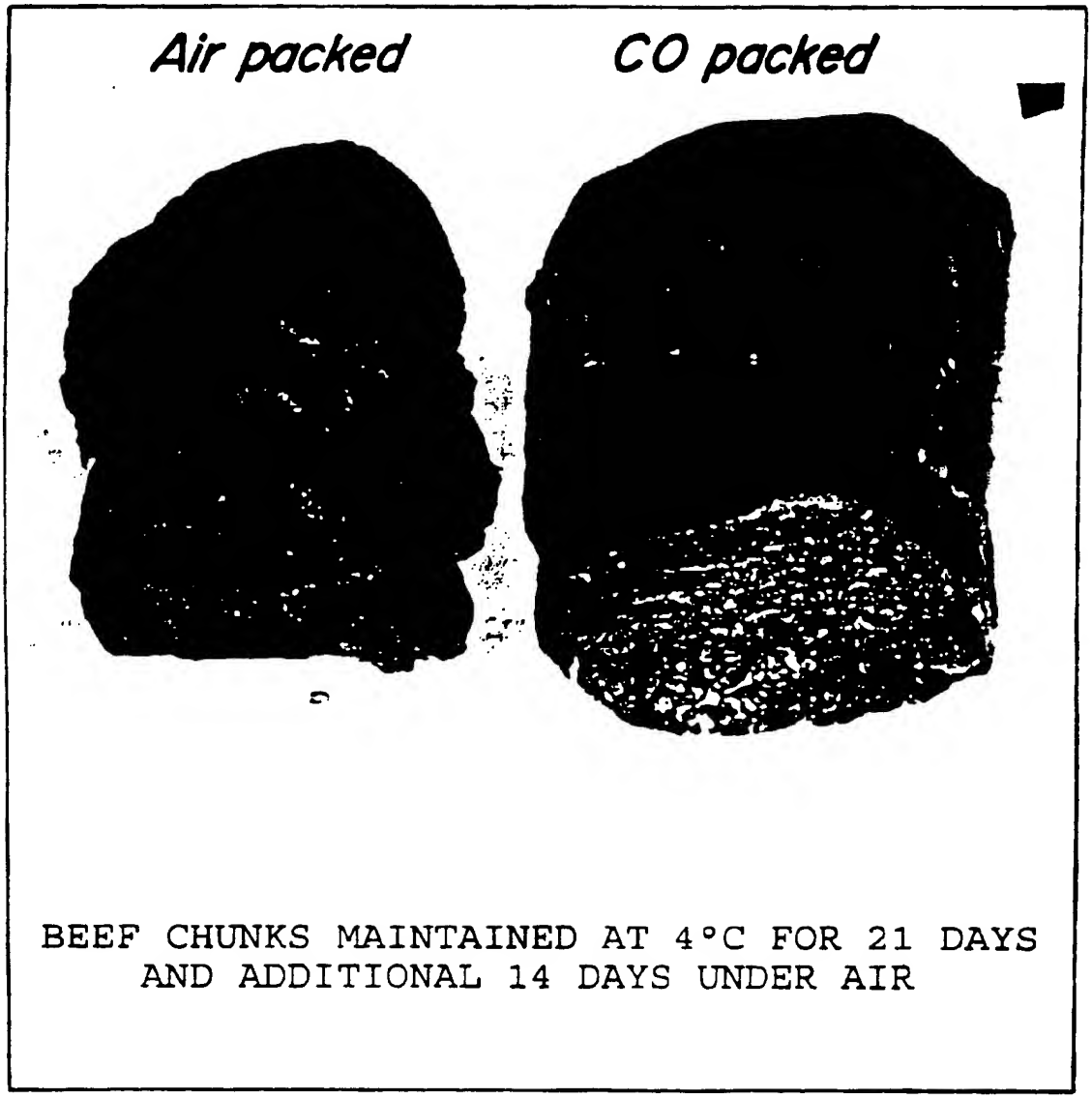
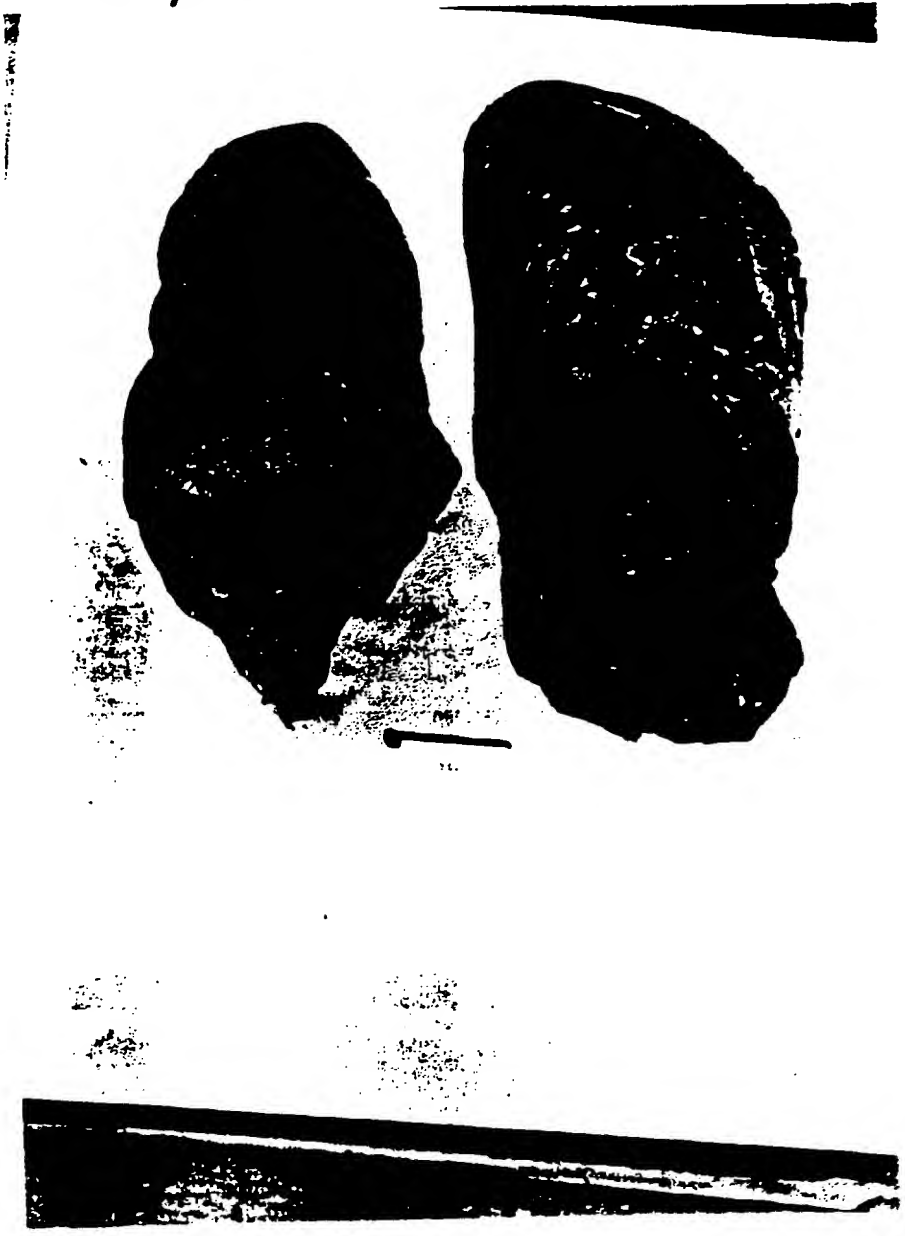

Air packed
CO packed
BEEF CHUNKS MAINTAINED AT 4°C FOR 21 DAYS
AND ADDITIONAL 14 DAYS UNDER AIR

Fig-5



BEEF CHUNKS MAINTAINED AT 4°C FOR 21 DAYS

RIGHT: CO PACKED
LEFT: AIR PACKED

Fig - 6

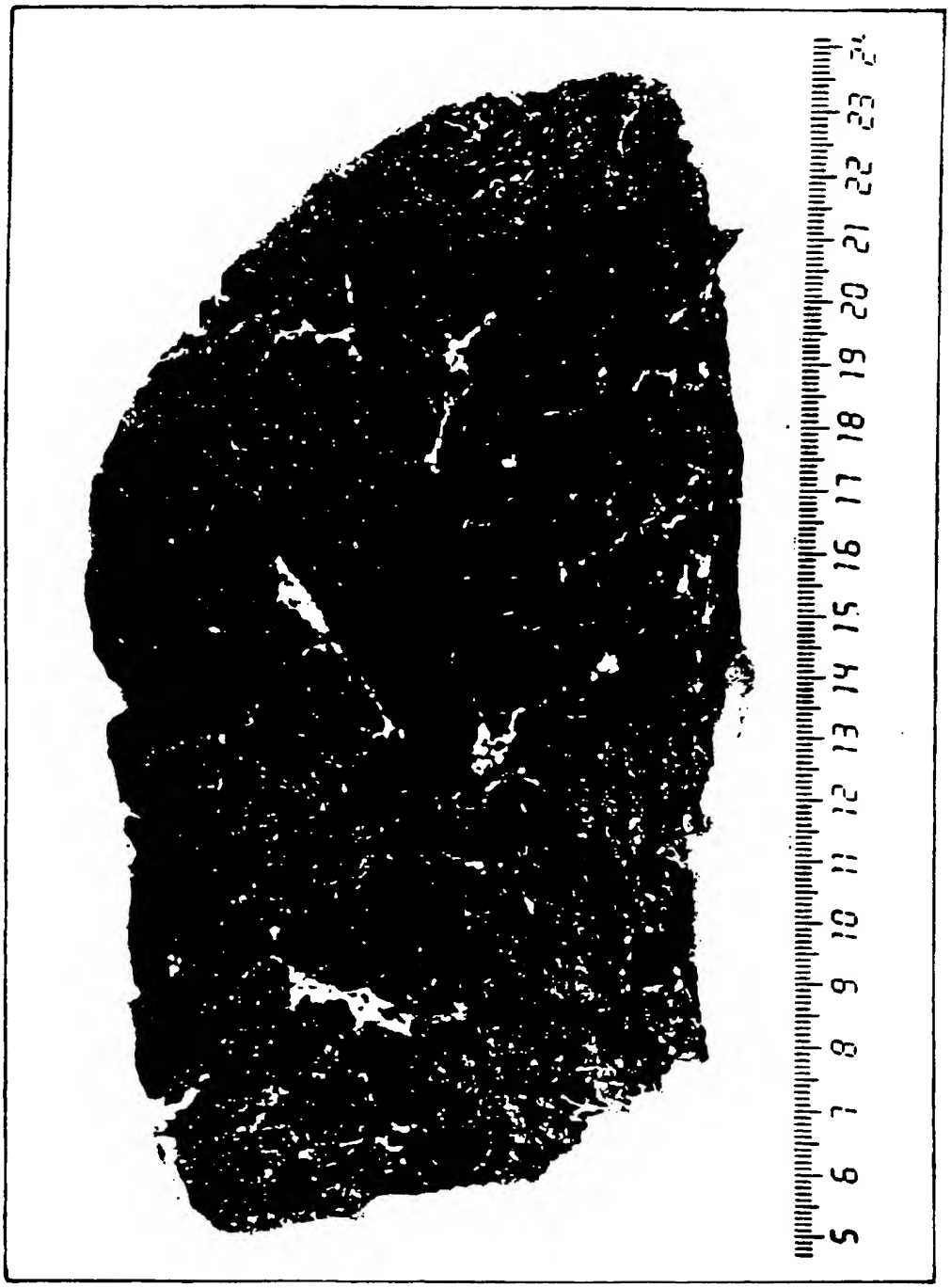


Fig-7

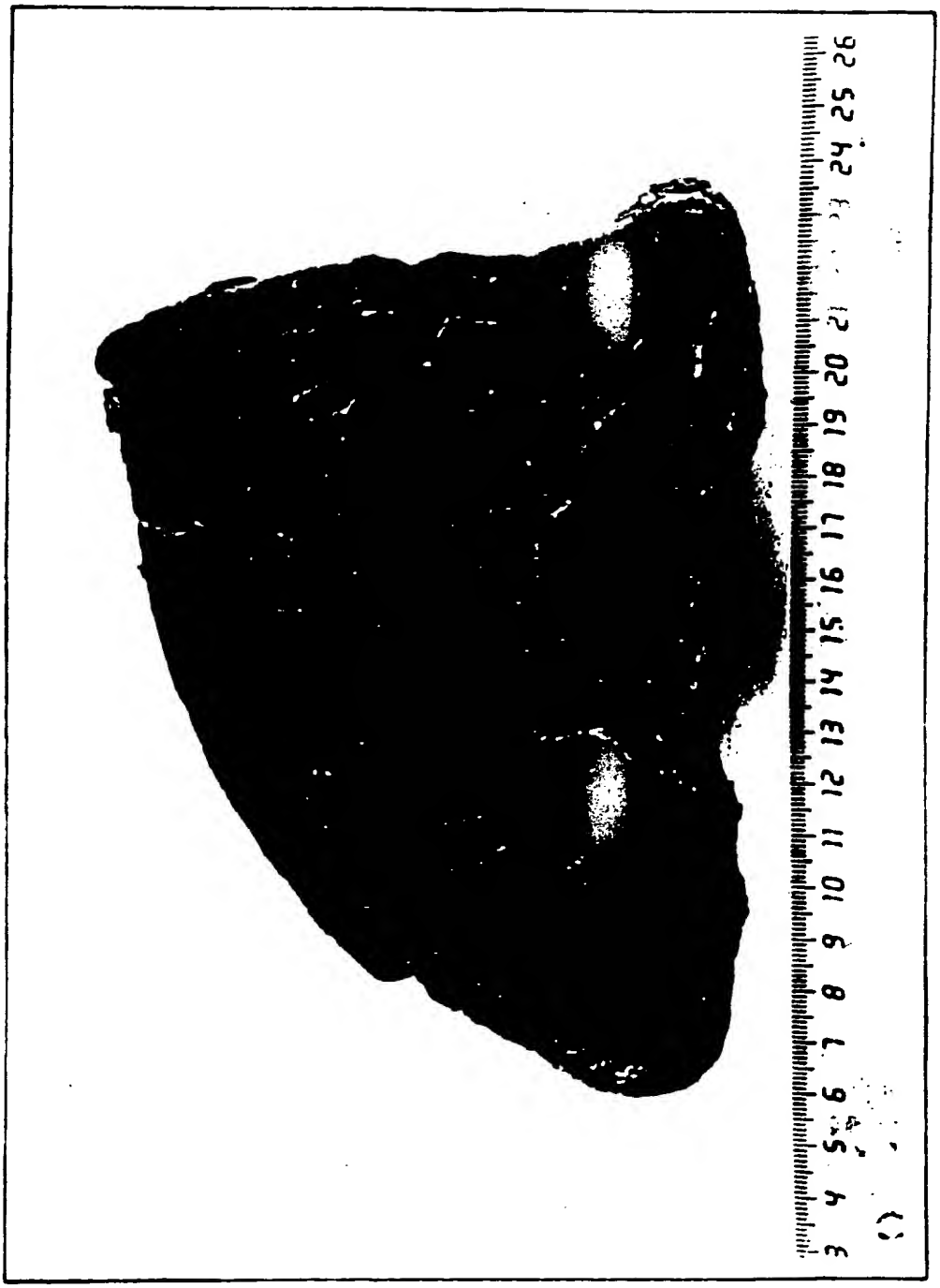


Fig - 8

Fig - 9

Fig - 10

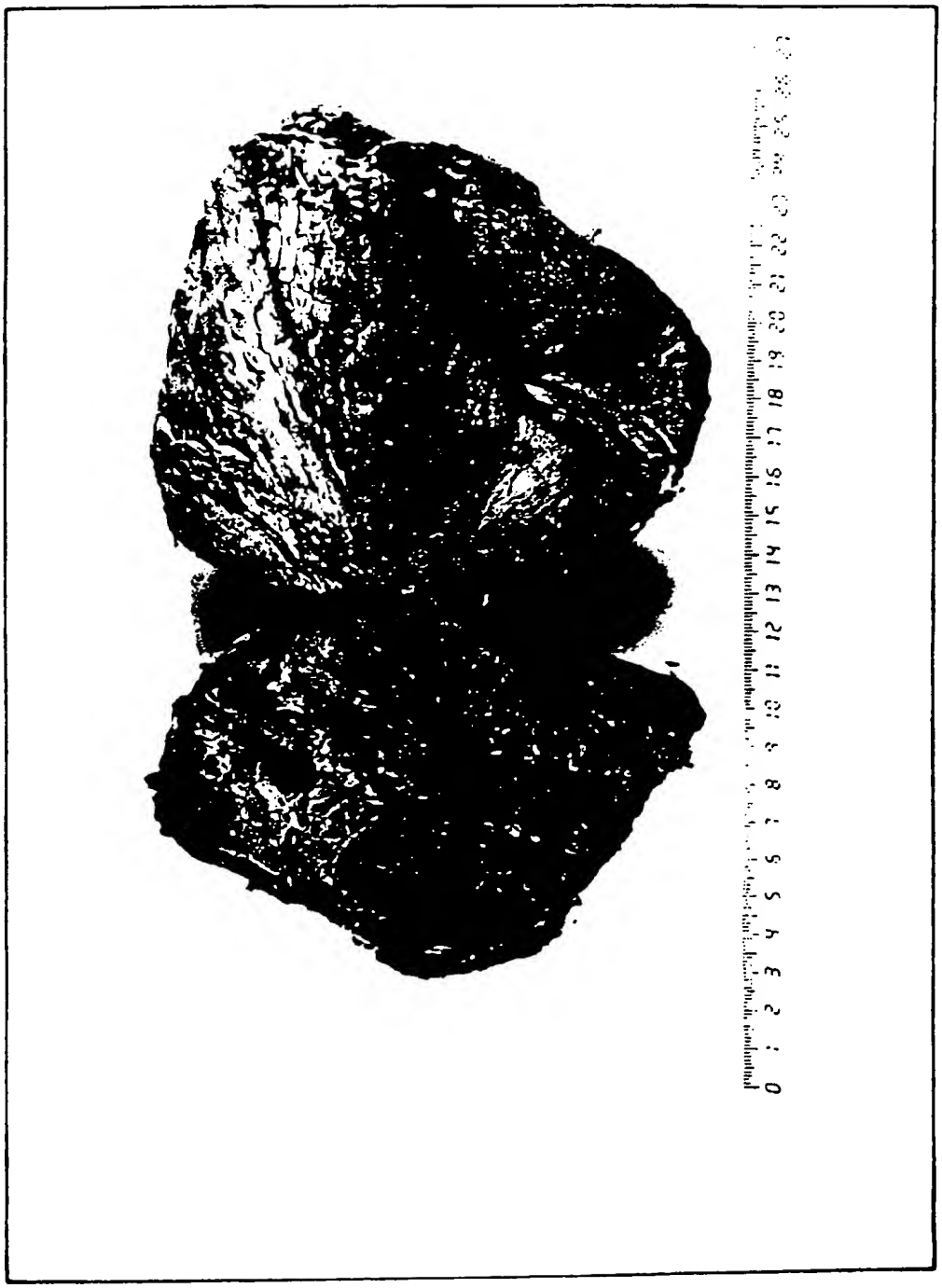


Fig - 11

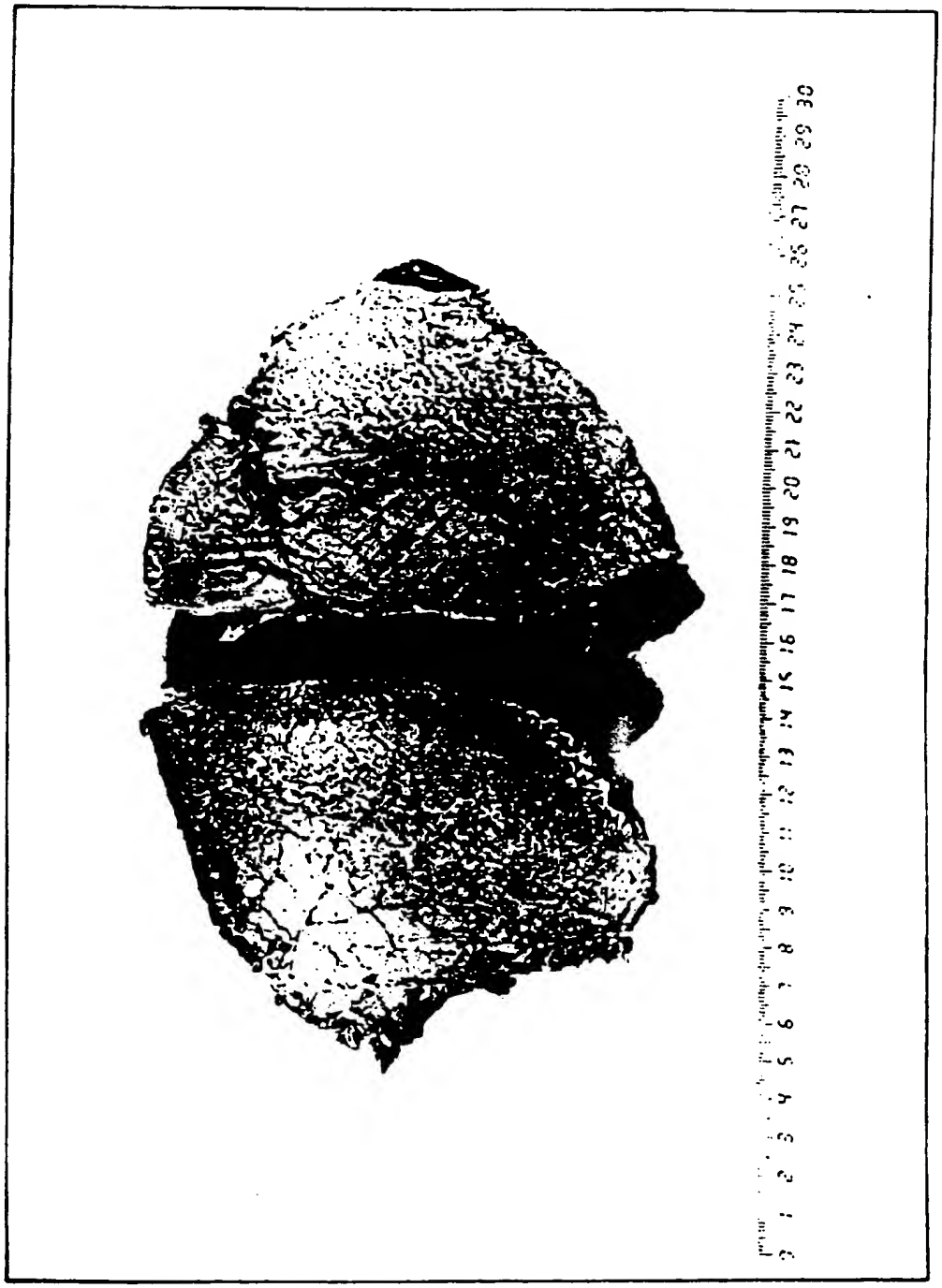
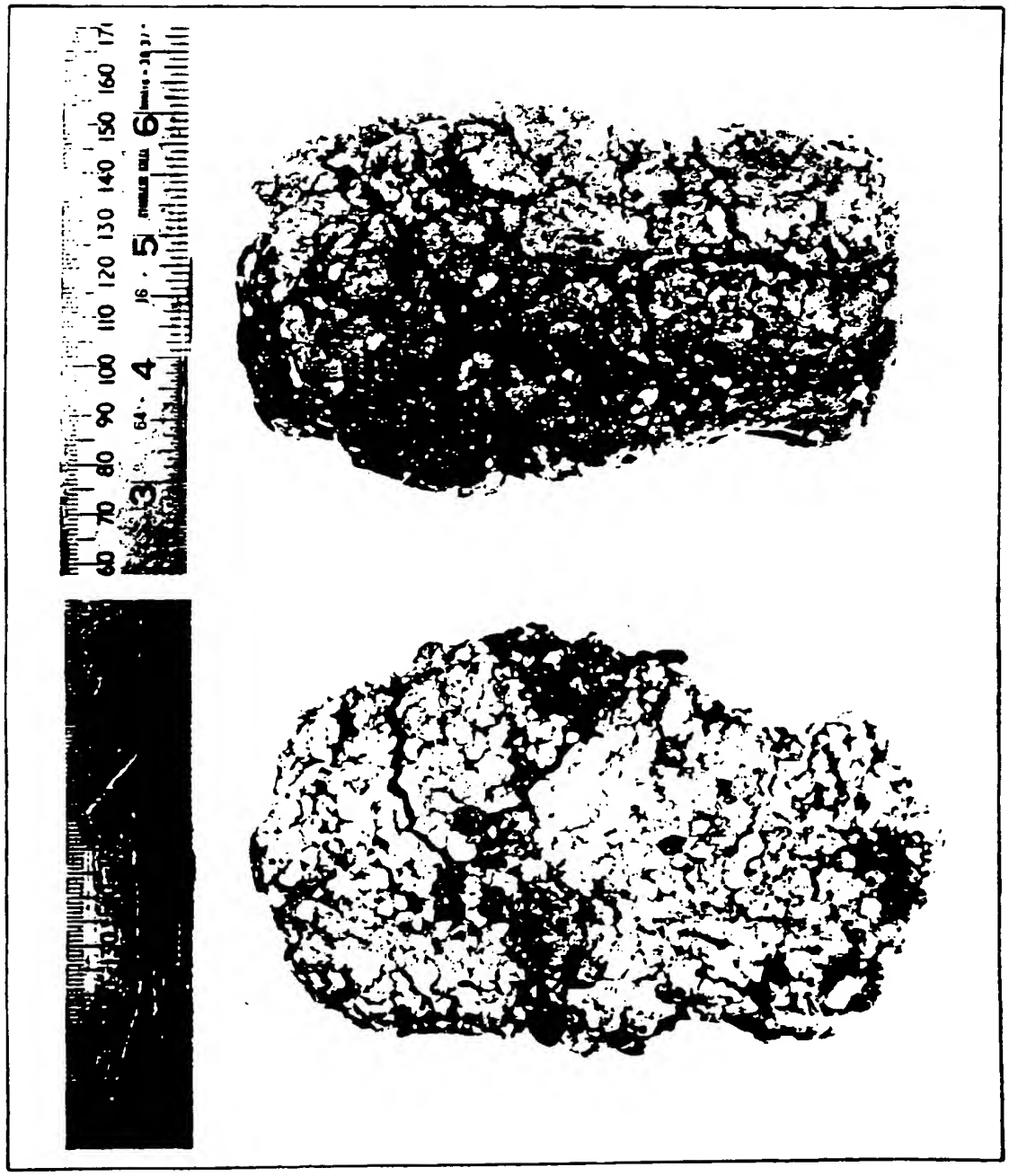


Fig - 12

Fig - 13



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05373

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B65B 31/02; A23L 3/3409
US CL :426/129, 264, 316, 418
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/129, 264, 316, 418

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CAN. INST. FOOD SCI. TECHNOL. J., VOL. 9 No. 3, issued 1976, CLARK et al, "Use of Carbon Monoxide for Extending Shelf-Life of Prepackaged Fresh Beef", pages 114-117, See entire document.	1-26
Y	J. OF FOOD QUALITY, v. 17(3), issued JUNE 1994, BREWER et al, "Carbon Monoxide Effects on Color and Microbial Counts of Vacuum-Packaged Fresh Beef Steaks In Refrigerated Storage", pages 231-244, See entire document.	1-26
Y	JP, A, 05-316939 (TADA) 03 DECEMBER 1993, See entire document.	1-26

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 09 JULY 1996	Date of mailing of the international search report 14 AUG 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer STEVEN L. WEINSTEIN Telephone No. (703) 308-0650

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05373

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	J. of Food Science, vol. 37, issued 1972, BESSER et al, "Changes In Quality and Nutritional Composition of Foods Preserved by Gas Exchange", pages 820-823, See entire document.	1-26
Y	AU, A, 214619 (TAMAYAMA ET AL), 13 OCTOBER 1992, See entire document.	1-26

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

extract both [illegible] and [illegible]. The extract

PATENT ABSTRACTS OF JAPAN

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A23L 3/3436

(21)Application number : **05-137405**

(22)Date of filing : **08.06.1993**

(71)Applicant : **TOPPAN PRINTING CO LTD**

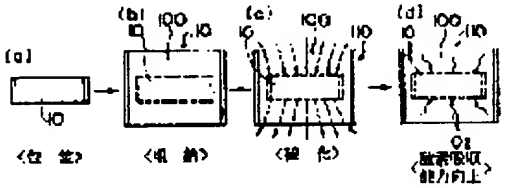
(72)Inventor : **TAKAI YUKA**
WADA KIYOSHI

(54) METHOD FOR STARTING OXYGEN ABSORPTION AND OXYGEN ABSORBENT USED THEREIN

(57)Abstract:

PURPOSE: To initially explosively develop oxygen absorbency by adding a specific external stimulus, such as magnetization, low-temp. treatment or vibration treatment, to the oxygen absorbent consisting of an iron compsn. as a base material.

CONSTITUTION: The iron compsn. (e.g. iron compsn. contg. residual austenite of ≥0.1% carbon content) is housed into an air permeable small bag 10, the specific external stimulus, such as magnetization, low-temp. treatment or vibration treatment, is added to the oxygen absorbent to initially explosively develop the oxygen absorbency. Namely, the oxygen absorbent is extremely low in the oxygen absorbency during storage thereof and initially explosively develops the oxygen absorbency by the external stimulus, such as magnetism, low temp. insulation or vibrating, at the time of use and, therefore, the handling during the storage and use of the oxygen absorbent is extremely easier than the conventional oxygen absorbent.



LEGAL STATUS

[Date of request for examination]

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[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報(A)　(11)特許出願公開番号

特開平6－343815

(43)公開日　平成６年(1994)12月20日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｂ０１Ｄ　53/14		Ｂ		
Ａ２３Ｌ　3/3436		５０１		

審査請求　未請求　請求項の数８　ＯＬ　（全７頁）

(21)出願番号　特願平5－137405

(22)出願日　平成５年(1993)６月８日

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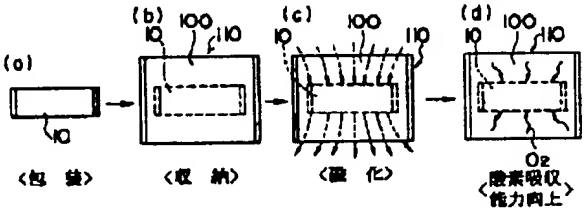
(72)発明者　和田　潔
東京都台東区台東一丁目５番１号　凸版印刷株式会社内

(54)【発明の名称】　酸素吸収開始方法及びこれに用いる酸素吸収剤

(57)【要約】

【目的】保管時には酸素吸収能力が極めて低く、使用時には特定の外的刺激によって酸素吸収能力が起爆的に発現する酸素吸収剤を開発する。

【構成】鉄組成物を基材とする酸素吸収剤を、磁性化、低温度処理又は振動処理などの特定の外的刺激によって、酸素吸収能力を起爆的に発現させる。



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【特許請求の範囲】

【請求項1】鉄組成物を基材とする酸素吸収剤に対する特定の外的刺激を加えることを特徴とする、酸素吸収開始方法。

【請求項2】鉄組成物を基材とする酸素吸収剤を磁化することを特徴とする、請求項1の酸素吸収開始方法。

【請求項3】鉄組成物の炭素量が0．1％以上であることを特徴とする、請求項2の酸素吸収開始方法。

【請求項4】鉄組成物を基材とする酸素吸収剤に、低温処理又は振動処理を行うことを特徴とする、請求項1の酸素吸収開始方法。

【請求項5】鉄組成物が、残留オーステナイトを含むことを特徴とする、請求項4の酸素吸収開始方法。

【請求項6】包装容器内に酸素吸収剤を封入した後に、外的刺激を与えることを特徴とする、請求項1ないし請求項5のいずれかに記載の酸素吸収開始方法。

【請求項7】請求項1又は2のいずれかに用いる酸素吸収剤であって、炭素量が0．1％以上である鉄組成物を基材とすることを特徴とする、酸素吸収剤。

【請求項8】請求項1又は4のいずれかに用いる酸素吸収剤であって、残留オーステナイトを含む鉄組成物を基材とすることを特徴とする、酸素吸収剤。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、食品や医薬品などの包装材料中に封入して使用する酸素吸収剤の酸素吸収開始方法及びこれに用いる酸素吸収剤に関するものである。

【0002】

【従来の技術】食品や医薬品などで、その保存雰囲気中の酸素の存在が好ましくない品物を保存する場合には、図4に示すように、ガスバリヤ性を有する包装材料（110）中に、その品物（50）と通気性を有する小袋（11）に入れられた酸素吸収剤（1）を共存させて密封する方法が、以前から行われていた。その酸素吸収剤は、酸素を吸収する性質をもつ組成物であり、鉄粉又は鉄化合物を主剤とする無機系のものと、アスコルビン酸塩やカテコールなどの複合炭水化物を用いた有機系のものとがあり、現在は、安全性や酸素吸収率及びコストなどから、鉄系化合物を主剤とするものが主流となっており、炭素量が0．08％のα鉄で体心立方構造を持つものや、炭素量が0．43％の炭素鋼でα鉄とセメンタイト（Fe，C）が層状になっているものなどが用いられていた。

【0003】

【発明が解決しようとする課題】しかしながら、酸素吸収剤は、その酸素吸収能力の発現を開始するのが、包装材料中に食品や医薬品などの品物と共に封入される時点であることが好ましく、封入以前に酸素吸収能力の発現が開始されると、封入以降の酸素吸収能力の低下の原因となった。このため、従来では、保存時に酸素吸収能力を発現させないように、バリヤ性の包装体で、酸素吸収剤を収納した通気性を有する小袋の上から二重に包装保管されていた。そして、保存しようとする食品や医薬品などの品物を収納した包装体に酸素吸収剤を封入する時に、前述の二重包装の外装を開封して酸素吸収剤を収納した小袋を取り出して使用していたが、取り出されてから品物を収納した包装体に挿入され、包装体が密封されるまでの時間の管理が必要となり、また、使用後に残った酸素吸収剤についたは、再度二重包装して保管しなければならず、その取扱いが煩雑であった。本発明は、酸素吸収剤の保管時には酸素吸収能力が極めて低く、使用時には特定の外的刺激によって酸素吸収能力が起爆的に発現し、保管時や使用時の取扱いがし易い酸素吸収剤を提供するものである。

2

【0004】

【課題を解決するための手段】第一の本発明は、鉄組成物を基材とする酸素吸収剤に対する特定の外的刺激を加えることを特徴とする酸素吸収開始方法である。

【0005】第二の本発明は、鉄組成物を基材とする酸素吸収剤を磁化することを特徴とする第一の本発明の酸素吸収開始方法である。

【0006】第三の本発明は、鉄組成物の炭素量が0．1％以上であることを特徴とする第二の本発明の酸素吸収開始方法である。

【0007】第四の本発明は、鉄組成物を基材とする酸素吸収剤に、低温処理又は振動処理を行うことを特徴とする第一の本発明の酸素吸収開始方法である。

【0008】第五の本発明は、鉄組成物が、残留オーステナイトを含むことを特徴とする、第四の本発明の酸素吸収開始方法である。

【0009】第六の本発明は、包装容器内に酸素吸収剤を封入した後に、外的刺激を与えることを特徴とする、第一の本発明ないし第五の本発明のいずれかに記載の酸素吸収開始方法である。

【0010】第七の本発明は、第一の本発明又は第二の本発明のいずれかに用いる酸素吸収剤であって、炭素量が0．1％以上である鉄組成物を基材とすることを特徴とする酸素吸収剤である。

【0011】第八の本発明は、第一の本発明又は第四の本発明のいずれかに用いる酸素吸収剤であって、残留オーステナイトを含む鉄組成物を基材とすることを特徴とする酸素吸収剤である。

【0012】上述に記載の酸素吸収剤の基材の鉄組成物は、表面積を向上するために、通常は微細粉、フレーク、微細粒のものを使用する。

【0013】また、基材の鉄組成物に、必要に応じては、酸素吸収能力の促進又は抑制、延命、消臭などの目的で、塩化ナトリウムや活性炭などの適宜の混合剤（添加剤）を混合（添加）しても良い。

【0014】

3

【作用】理論的には、証明されていないが、鉄を磁化するとさびが進行し易い。本発明は、この現象を酸素吸収剤に利用したものであるが、発明者らの試験では、表1に示すように、炭素量が大きい方が磁力の保持性や酸化＊

4

＊能力が大きいことを見出している。

【0015】

【表1】

鉄中の炭素量とその特性

鉄中炭素量(%)	磁化に必要な磁力	磁力の保持性	酸化能力
0．0～1．0	低　い	低　い	低　い
0．1～2．4	高　い	高　い	高　い

【0016】また、残留オーステナイトを含有した鉄は、図3に示すように、保冷や振動などの外的刺激によって、組成中の残留オーステナイト（a）がマルテンサイト（b）へ変化し、表2に示すように、酸化能力が高くなる。そしてこの残留オーステナイトの生成量は、鉄に含まれる炭素量に関係し、発明者らの試験では、鉄に含まれる炭素量が0．66％のときは残留オーステナイ※トの生成量は0％であるが、炭素量が1．2％のときは残留オーステナイトの生成量は60～65％であった。炭素量を1．2％以上に増やしても、残留オーステナイトの生成量は、炭素量が1．2％のときと比較してあまり増加はなかった。

【0017】

【表2】

組成状態とその特性

組成状態	磁　性	酸化能力
残留オーステナイト	非　磁　性	非常に低い
マルテンサイト	磁　性	高　い

【0018】

【実施例】鉄は、酸化するときに、下記の化学反応式に示されるように、水分を必要とする。

鉄の酸化反応：$Fe \rightarrow Fe^{2+} + 2e^-$

$1/2\ O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$

$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2$

$Fe(OH)_2 + 1/4\ O_2 + 1/2\ H_2O \rightarrow Fe(OH)_3$

【0019】このため、本発明の鉄組成物の酸素吸収剤の機能を十分に発揮させるには、水分を補給させる必要がある。この方法としては、水分を酸素吸収剤の組成物に直接添加したり、品物自体の水分を利用したり、または、水分を吸収した吸水性樹脂を添加する方法などがある。なお、吸水性樹脂としては、アクリル酸－ビニルアルコール共重合体、アクリル酸ソーダ重合体、アクリル酸ソーダーアクリルアミド共重合体、ポリエチレンオキサイド変成物、デンプングラフト高分子及びセルロース誘導体などが使用できる。

【0020】＜実施例1＞まず、炭素量が0．12％の微細粉の鉄1g、微細粉の塩化ナトリウム2g、1gの水を吸収したアクリル酸ビニルアルコール共重合体1．1gの比率で混合した本実施例の鉄組成物の酸素吸収剤を作製し、図4（a）に示したように、この酸素吸収剤（11）4．1gを紙／有孔ポリエチレン（開口径0．2mm，開口率1．0％）構成の通気性の小袋（11）に収納した。

【0021】酸素吸収剤の実用時には、図4（b）に示したように、保存雰囲気中に酸素の存在が好ましくない品物（50）と一緒に酸素吸収剤を収納する小袋（10）をガスバリヤ性を有する包装体（100）中に封入し、この包装体をマグネットプレート上に放置するか、マグネットドームを通過させて酸素吸収剤を磁化して、その酸素吸収性を起爆的に活性化するものであるが、本実施例においては、作製した本実施例の酸素吸収剤の特

5

性を評価するために、密閉容器内に前記作製した酸素吸収剤を収納した小袋を封入し、マグネットドームを通過させて酸素吸収剤を磁化して、酸素吸収剤の酸素吸収性を起爆的に活性化させた後、２０°Ｃの雰囲気中に保って、１２時間、２４時間及び４８時間の経時における酸素吸収量をそれぞれ測定した。この評価結果を、表３に＊

6

＊示したが、４８時間経時で酸素吸収量は、３１４ｍｌであり、本実施例の酸素吸収剤は、良好な酸素吸収性を示した。

【００２２】

【表３】

酸素吸収剤の組成及び酸素吸収能評価結果

酸素吸収剤の組成				酸素吸収能力評価結果		
鉄組成物	促進剤	水分供給	外的刺激	12Hr後	24Hr後	48Hr後
炭素量０．１２％の鉄（微細粉） １ｇ	塩化ナトリウム（微細粉） ２ｇ	ｱｸﾘﾙ酸ﾋﾞﾆﾙｱﾙｺｰﾙ共重合体（吸水量１ｇ） １．１ｇ	磁化 １０秒	２９８ml	３０９ml	３１４ml

【００２３】＜実施例２＞まず、炭素量が１．２％で残存オーステナイトが６０％の微細粉の鉄１ｇ、微細粉の塩化ナトリウム２ｇ、１ｇの水を吸収したアクリル酸ビニルアルコール共重合体１．１ｇの比率で混合した本実施例の鉄組成物の酸素吸収剤を作製し、この酸素吸収剤４．１ｇを、実施例１と同様の紙／有孔ポリエチレン構成の通気性の小袋に収納した。

【００２４】そして、実施例１と同様に、密閉容器内に前記作製した酸素吸収剤を収納した小袋を封入し、－５°Ｃの雰囲気に５時間保冷して酸素吸収剤の酸素吸収性を起爆的に活性化させた後、２０°Ｃの雰囲気中に保って、１２時間、２４時間及び４８時間の経時における酸素吸収量をそれぞれ測定した。この評価結果を、表４に示したが、４８時間経時で酸素吸収量は、２８７ｍｌであり、本実施例の酸素吸収剤は、良好な酸素吸収性を示した。

【００２５】

【表４】

7 8

酸素吸収剤の組成及び酸素吸収能評価結果

酸素吸収剤の組成				酸素吸収能力評価結果		
鉄組成物	促進剤	水分供給	外的刺激	12Hr後	24Hr後	48Hr後
炭素量が1．2％で残留オーステナイトが60％の鉄（微細粉） 1g	塩化ナトリウム（微細粉） 2g	アクリル酸ビニルアルコール共重合体（吸水量1g） 1．1g	保冷（－5°C） 5時間	253ml	266ml	287ml

【0026】＜実施例3＞まず、炭素量が1．2％で残存オーステナイトが60％の微細粉の鉄1g、微細粉の塩化ナトリウム2g、1gの水を吸収したアクリル酸ビニルアルコール共重合体1．1gの比率で混合した本実施例の鉄組成物の酸素吸収剤を作製し、この酸素吸収剤4．1gを、実施例1と同様の紙／有孔ポリエチレン構成の通気性の小袋に収納した。

【0027】そして、実施例1と同様に、密閉容器内に前記作製した酸素吸収剤を収納した小袋を封入し、10秒間の振動を与えて酸素吸収剤の酸素吸収性を起爆的に活性化させた後、20°Cの雰囲気中に保って、12時間、24時間及び48時間の経時における酸素吸収量をそれぞれ測定した。この評価結果を、表4に示したが、48時間経時で酸素吸収量は、343mlであり、本実施例の酸素吸収剤は、良好な酸素吸収性を示した。

【0028】

【表5】

酸素吸収剤の組成及び酸素吸収能評価結果

酸素吸収剤の組成				酸素吸収能力評価結果		
鉄組成物	促進剤	水分供給	外的刺激	12Hr後	24Hr後	48Hr後
炭素量が1．2%で残留オーステナイトが60%の鉄（微細粉） 1g	塩化ナトリウム（微細粉） 2g	アクリル酸ビニルアルコール共重合体（吸水量1g） 1．1g	振動 10秒間	312ml	336ml	343ml

【0029】

【発明の効果】本発明の酸素吸収剤を用いると、酸素吸収剤の保管時には酸素吸収能力が極めて低く、使用時に磁気、保冷や振動などの外的刺激によって酸素吸収能力が起爆的に発現するため、酸素吸収剤の保管時や使用時の取扱いが従来の酸素吸収剤に比較して極めて容易となる。

【図面の簡単な説明】

【図1】本発明の酸素吸収剤を小袋に収納して使用した時の、実施例1における使用過程を示す説明図である。

【図2】本発明の酸素吸収剤を小袋に収納して使用した時の、実施例2及び実施例3における使用過程を示す説明図である。

【図3】鉄に含有する残存オーステナイトが保冷や振動によって、マルテンサイトに変化する状態を示す説明図である。

【図4】（a）酸素吸収剤を収納した通気性の小袋の断面図である。

（b）パリヤ性の包装体に、品物と酸素吸収剤を収納した小袋とを一緒に封入した状態を示す説明図である。

【符号の説明】

1……酸素吸収剤

10，20……酸素吸収剤を収納した通気性の小袋

11……通気性の小袋

50……品物

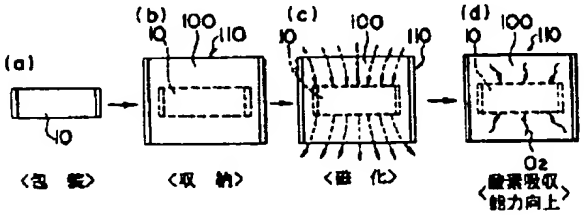
100，200……パリヤ性の包装体

110，210……品物と酸素吸収剤とを封入したパリヤ性の包装体

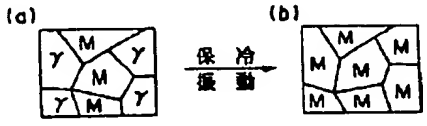
γ……オーステナイト

M……マルテンサイト

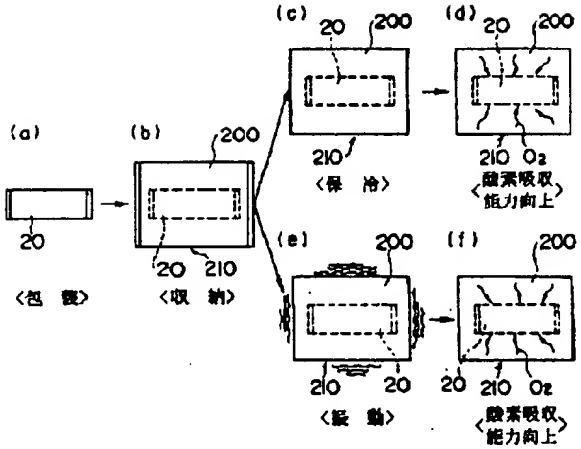
【図1】



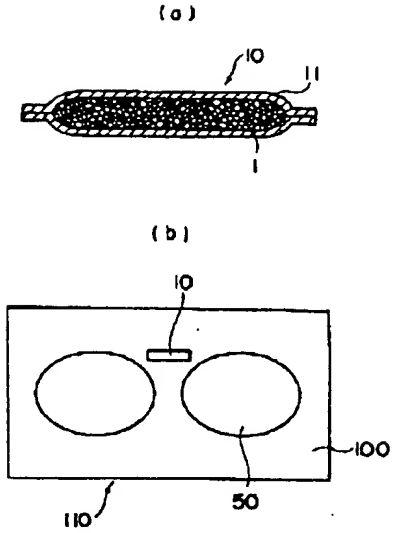
【図3】



【図2】


(a)
(b)
(c)
(d)
(e)
(f)
200
20
210
O2
〈包 装〉
〈収 納〉
〈保 冷〉
〈酸素吸収能力向上〉
〈振 動〉
〈酸素吸収能力向上〉

【図4】


(a)
10
11
1
(b)
10
100
50
110

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(54) PACKAGING FOR MEAT AND OTHER FOODSTUFF

VERPACKUNG FÜR FLEISCH ODER ANDERE NAHRUNGSMITTEL

CONDITIONNEMENT DE LA VIANDE ET D'AUTRES PRODUITS ALIMENTAIRES

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Description

TECHNICAL FIELD

[0001] Th present invention is directed to the field of packaging. More specifically it deals with carbon dioxide releasing systems in conjunction with systems capable of absorbing oxygen. Bag and sachets incorporating such components are also discussed. Modified packages associated with the use of such systems are also discussed as are methods of use associated with the present invention.

BACKGROUND ART

[0002] The description of the present invention will be discussed predominantly in relation to meat products whose associated packaging problems are typical of those which the present invention considers. However it should be appreciated that the present invention can also be applied to other foodstuffs and articles to be packaged.

[0003] More specifically, and for simplicity of description, the problems associated with chilled and fresh meat will be discussed as the problems associated with these products are perhaps the most demanding. Consumer perception is that a red meat product is a fresh meat product and therefore preferable to discoloured products. Unfortunately, for fresh and chilled meats, storage under conditions where oxygen is present results in gradual browning of the meat. While in many cases (short term storage) the product is still acceptable, the consumer is deterred by the brownish appearance of the meat which they associate with a spoiled product.

[0004] Where there is longer term storage of meat products, the presence of oxygen can result in not only the browning of the meat but subsequent spoilage. Accordingly packages for long term storage of meat generally comprise an oxygen impermeable barrier film. Often the packages are evacuated or packed under a modified atmosphere.

[0005] Vacuum packaging is not generally considered appropriate for the retail display of chilled red meat, because of the meat's purple coloration. Low oxygen modified atmosphere systems are also not appropriate for the same reasons.

[0006] High oxygen/low carbon dioxide modified atmosphere systems are successfully used for retail cuts of red meat, but in this case, the storage life is low due to oxygen spoilage.

[0007] Recently a packaging system known as low oxygen/high carbon dioxide packaging has become very popular. The system has been directed mainly at non-retail ready markets, as the primal cuts used require further processing into consumer portions. Also the meat requires re-exposure to oxygen to resume a red rather than purple colouration.

[0008] It has been found that chilled meat packaged under carbon dioxide is resistant to spoilage by aerobic bacteria. Anaerobic bacteria which may still survive under Carbon dioxide do not flourish below 2°C, which is above the storag temperature of most chilled meat products. Evidence suggests that a relatively high concentration of carbon dioxide will actively suppress the bacterial growth - the shelf life of Carbon dioxide packaged meat is thus much longer than for vacuum packed meat.

[0009] Like the vacuum packed product, meat stored under carbon dioxide will rebloom on exposure to oxygen, giving the red coloration which consumers associate with freshness. However, it is also believed that the display life, in the oxygenated state, of carbon dioxide packaged meat is longer than that of vacuum packed meat. This may be associated with the low oxygen concentration throughout the product lifetime, which is a key requirement of the carbon dioxide process.

[0010] The use of low oxygen/high carbon dioxide packaging is well known, as is the use of oxygen absorbing compositions with meat products. Combinations of the two systems are also known. However, many problems remain.

[0011] For instance systems which release carbon dioxide are well known. Of note is the work of Benedict, Strange, Palumbo and Swift (Journal of Agricultural and Food Chemistry, 23 (6) *1202-1208* 1975). Gas permeable sachets consisting of citric acid and sodium bicarbonate were added to retail packages of meat and the carbon dioxide released helped to extend shelf life. Codimer also patented a system where carbon dioxide and/or oxygen were generated in a package from the reaction of citric acid with sodium bicarbonate and/or sodium perborate (EP O 128 795 (1984)).

[0012] A number of other systems also appear in the prior art which both absorb oxygen and liberate carbon dioxide. These systems were designed to replace the oxygen absorbed from within the head space of the package with high levels of carbon dioxide. For example, Toppan claims highly specific compositions such as:

100 parts ferrous chloride
20-100 parts sodium bicarbonate
5-50 parts water supplying substance
0-10 parts absorbent
0-70 parts iron powder

[0013] No examples or disclosure is provided within this patent which produce large amounts of carbon dioxide and absorb small amounts of oxygen (US 4,384,972 (1983)).

[0014] Mitsubishi describe a system where the amount of carbon dioxide generated may be independent of the amount of oxygen absorbed. However the teaching of this specification limits the amount of carbon dioxide produced per mole of oxygen absorbed (US

4,762,722 (1988)).

[0015] However the prior art fails to address the problems associated with the packaging of meat, and especially the packaging of meat in retail ready tray-based packages. The Mitsubishi system was intended to be used for sealing a package without evacuation or gas flushing and in its place greater than two moles of carbon dioxide per mole of oxygen absorbed was said to lead to pack deformation. At the time of this patent the prior art also considered that carbon dioxide gas flushing when packaging meat resulted in unwanted browning. Accordingly the art considered, and this is reflected in the limitations of the art, that excessive carbon dioxide, such as would also result through carbon dioxide gas flushing, was undesirable. However it has since been found that this browning is not due to carbon dioxide but rather to the incomplete removal of oxygen from within the package and may be a temporary condition, depending upon the levels of enzyme activity which relates to time post mortem.

[0016] Other prior art, such as EP O 527,228 (Toppan) describes oxygen absorbers/carbon dioxide generators such as mixtures of ascorbic acid and ferrous chloride. However the quantity of carbon dioxide released is dependent upon the amount of oxygen absorbed as well as on the pH of the composition. The pH may be determined by the addition of an alkali such as sodium bicarbonate, sodium carbonate of calcium hydroxide. However this disclosure is targeted at applications where a set amount of carbon dioxide and nitrogen is required within a container (e.g. containers for growing bacteria samples). This, and the known prior art, fail to address the need to package meat for extended periods of time, and be able to regenerate or preserve a consumer acceptable red colouration at the retail level. In addition, there is a need, for retail ready packs, to prevent deformation of a pack due to variations in the internal atmosphere. These problems arise due to the fact that meat will absorb large quantities of carbon dioxide, generally within the first 48 hours of exposure. As this absorption process proceeds, the internal pressure of a package is reduced, unless there is a sufficient excess of carbon dioxide to completely saturate the meat, and there is a suitable mechanism by which the volume of the package may contract.

[0017] If meat is placed on a conventional sized tray, evacuated, gas flushed with carbon dioxide and then sealed under a barrier film, severe distortion will occur as the carbon dioxide is absorbed and the internal pressure of the system is reduced. This is because the volume of the tray cannot contract in a controlled manner like that of a bag, and because insufficient carbon dioxide is present to compensate for what is absorbed by the meat.

[0018] This problem becomes more noticeable as an attempt is made to keep a high product volume in relation to the volume of the package. High product to package volume systems are used conventionally (i.e. PVC overwrapped product on an expanded polystyren tray) for retail display of meat cuts.

[0019] Large volume packages containing a low volume of product are resented by consumers, who associate them with excessive packaging and waste. They are also unpopular with retailers as they occupy excessive shelf space, and also with exporters/distributors because of their high volume and low weight.

[0020] It would therefore be desirable to provide a system whereby the long storage life and display life of low oxygen/high carbon dioxide packaging could be applied to individual tray or bag wrapped systems, whilst maintaining the low volume associated with the conventional retail meat packaging systems.

[0021] It would also be desirable to modify the existing low oxygen/high carbon dioxide packaging in such a manner that the absorption of carbon dioxide by the meat cuts is matched by the generation of carbon dioxide by chemical means. The existing packaging system involves first wrapping the meat cuts in absorbent material, and then placing a number of them in a carton lined with a high barrier bag. The bag is then evacuated, flushed with carbon dioxide and sealed. Frequently the carton is not sealed for a further 24 hours so that most of the carbon dioxide can be absorbed and the final package volume is relatively low. For beef, one litre of carbon dioxide is recommended for each kilo of meat. For lamb, 1.5 litres per kilo is recommended. This delay in sealing the cartons is a source of frustration at the meat plants.

[0022] When meat is vacuum packed "drip" is drawn to the surface and will accumulate in areas where there is no intimate contact. This detracts from the appearance of the product.

[0023] It would also be desirable to extend this concept to a variety of non meat products.

[0024] It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

SUMMARY OF THE INVENTION

[0025] The present invention consists in a method of packaging meat or other foodstuffs in a carbon dioxide rich, low oxygen package environment comprising providing a food package of a gas barrier material, placing a food product within said food package, placing in said package with said food product a carbon dioxide generating material and an oxygen removing material, and sealing said package, said carbon dioxide material generating carbon dioxide in a volume not dependent upon the removal of oxygen and greater than twice the mole ratio of oxygen removed by said oxygen removing material.

[0026] According to a feature of the invention, sufficient carbon dioxide generating material is included to release at least 0.1 litre of carbon dioxide, at STP, per kilogram of packaged meat.

[0027] According to another featur of the invention, sufficient oxygen removing material is included to maintain an oxyg n level, within the sealed package of 500 ppm or less throughout the storage life which may be for a period of at least 10 weeks from packaging.

[0028] According to another feature of the invention, the foodstuff is positioned within a tray of an oxygen barrier material, and the tray covered with an oxygen barrier film layer, the carbon dioxide producing and oxygen removing materials being included within the covered tray before sealing.

[0029] The present invention further consists in a food package for meat or other foodstuffs comprising a sealed enclosure of a gas barrier material, a food product confined in said enclosure, and a carbon dioxide generating material and an oxygen removing material also confined in said enclosure, said carbon dioxide generating material and said oxygen removing material being capable, over time, of removing oxygen from the atmosphere within said enclosure to provide a low oxygen environment therein and of generating carbon dioxide in a volume not dependent upon the removal of oxygen (see US-A-4 762 722) characterised in that the volume of carbon dioxide generated is greater than twice the mole ratio of oxygen removed to provide a carbon dioxide rich environment within said enclosure.

[0030] According to a feature of the invention, carbon dioxide producing, and oxygen removing, materials are present in the form of one or more sachets or inserts positioned within the sealed enclosure.

[0031] According to another feature of the invention, the package contents are separated from the carbon dioxide generating and oxygen removing materials by an oxygen and carbon dioxide permeable layer.

[0032] According to another feature of the invention, there is present an oxygen barrier seal overlying an oxygen permeable portion of the package, the removal of which allows permeation of oxygen through the oxygen barrier or impermeable layer.

[0033] The present invention also consists in a method of packaging meat or other foodstuffs in a carbon dioxide rich, low oxygen package environment comprising providing a food package including an outer enclosure of a gas barrier material and an interior member of a gas permeable material dividing the outer enclosure into two interior spaces, placing a food product in one of said interior spaces within said outer enclosure, placing a carbon dioxide generating material and an oxygen removing material in the other of said interior spaces within said outer enclosure such that said gas permeable member is between the food product and said carbon dioxide generating material and said oxygen removing material, and sealing said outer enclosure, said carbon dioxide generating material generating carbon dioxide, over time, in a volume not dependent upon the removal of oxygen and greater than twice the mole ratio of oxygen removed by said oxygen removing material.

[0034] According to another feature of the invention, the sealed enclosure comprises an oxygen impermeable tray into which foodstuff is placed and an overlying oxygen barrier film sealing the mouth of the tray, ther being included within the enclosure a carbon dioxide generating material and an oxygen removing material, the arrangement being such that the production of carbon dioxide is not dependent upon the removal of oxygen.

[0035] According to another feature of the invention, the package comprises an inner sealed oxygen and carbon dioxide permeable packet, into which the foodstuff is sealed, and positioned within a sealed enclosure comprising a bag of gas barrier material.

[0036] A problem with foodstuffs such as meat is that they can absorb large quantities of carbon dioxide. This can cause problems with packaging, and particularly the buckling of retail ready packs due to reduced internal pressure resulting from carbon dioxide absorption. Some other problems have been mentioned previously. One aspect of the present invention seeks to solve this problem by including within the package means for producing a relatively large volume of carbon dioxide while at the same time allowing for the absorption of residual oxygen from packaging, and preferably also any oxygen which permeates into the package throughout its normal lifetime. This may be addressed by including within the package means of generating carbon dioxide and absorbing oxygen. Ideally the amount of carbon dioxide generated is independent of the amount of oxygen absorbed. Generally also, substantially greater carbon dioxide generating capacity is provided for than oxygen removal capacity. In preferred embodiments sufficient materials are included to generate more than two moles of carbon dioxide for each mole of oxygen able to be absorbed. In many cases preferred embodiments will comprise much higher ratios.

[0037] Most embodiments of the present invention will involve the use of means for liberating or evolving carbon dioxide within a package of articles, and in many instances will rely upon a chemical component or system which is able to release carbon dioxide over a period of time. The generation of carbon dioxide within the package can address the problems associated with its absorption by meat or other articles. It is envisaged that in most cases the package will be flushed or sealed under carbon dioxide during packaging. The carbon dioxide generated within the package is generally to counteract absorption by the meat or other articles - an equally serious problem would be over inflation which ruptured seals of the package. Through this internal generation of replacement carbon dioxide for that which is absorbed, curling of trays (for instance) can be minimised if not totally eliminated.

[0038] Accordingly it is preferable that carbon dioxide releas is relativ ly slow over a continuing period of time to prevent over inflation of the package and possible release of carbon dioxide through the package

material due to an excessive internal pressure. In most cases the rate of carbon dioxide releas should approximate to the rate of carbon dioxide absorption by the packaged contents so that an approximate and d sired internal pressure within the package is maintained. For most meats the bulk of carbon dioxide absorption will be within the first 24 hours and it may be desirable to tailor carbon dioxide release to occur predominantly over this period. There will often be an advantage in the slow but continued carbon dioxide release over a longer period to compensate for losses of Carbon dioxide permeating through the film.

[0039] The rate of carbon dioxide release may be influenced by a variety of methods. For instance, chemical system may be chosen which will, when activated, release carbon dioxide at the appropriate rate. Another method is to make the rate of release of carbon dioxide responsive, or triggerable by, some condition within the package of articles. This condition might be the presence of moisture. Alternatively a system responsive to other stimuli could be used. Stimuli may include light or electromagnetic radiation in the visible and/or near visible regions, and/or electromagnetic radiation in other regions such as the RF, microwave, IR, and UV regions.

[0040] Another method is to contain the carbon dioxide evolving materials in a bag or container which limits or controls the rate of ingress of materials triggering carbon dioxide release, or to which the rate carbon dioxide release is responsive to. Secondly the bag or container may control the release of Carbon dioxide evolved within the bag or container.

[0041] A further method is to use components whose rate of generation or evolution of carbon dioxide are proportional to the internal pressure of the package. Such materials could be relied upon to maintain an approximate and desired internal pressure of carbon dioxide within the package. This could include the use of substances reversibly adsorbing carbon dioxide and these substances may be combined with other carbon dioxide generating systems such as described herein.

[0042] In addition to carbon dioxide evolution, it is desirable for there to be components or a system to remove oxygen which may be present in, or enter the package over time. Most embodiments of the present invention will incorporate such components or systems as even oxygen barrier films will allow the ingress of oxygen over a period of time (such as the period for which chilled meat is often stored). In an example to be given later, it will be shown that the absence of any oxygen removing substance or system will, in some cases, result in a higher than optimum level of oxygen being present in the package.

[0043] A wide range of oxygen absorbing or adsorbing compounds and systems are known. Whether the oxygen is absorbed or adsorbed or otherwise removed is not particularly relevant - the main aim is to ensure that there is not a level of free oxygen which could adversely affect the contents of the package.

[0044] The prior art has also investigated the use of substances and systems which consume fr oxygen in a reaction liberating carbon dioxide. Whil such systems may be included within th present invention, it should be appreciated that such systems should not be relied upon for the sole evolution of carbon dioxide. As the oxygen levels present within a package are relatively low, such systems will be unable to produce sufficient carbon dioxide to satisfy initial absorption by the packaged meat or article. Accordingly, such systems would only be useful for providing a perpetual and low volume supply of carbon dioxide during the life of the package (due to the low volumes of oxygen permeating through the package material) and thus higher volume carbon dioxide evolving systems should be relied upon.

[0045] The present invention may also include the use of water or moisture absorbing and/or adsorbing substances. This may be useful in the removal of fluids or excess humidity within the package. However, where these are combined with moisture responsive carbon dioxide evolving systems (such as the acid and carbonate systems to be described later), the affinity and capacity for moisture removal should not be such that the carbon dioxide evolution is not triggered by moisture present in the package. In some cases it may be useful to rely upon hygroscopic or deliquescent materials to draw moisture into the package yet allow sufficient moisture to be available for initiating the carbon dioxide evolution process.

[0046] The present invention may also include the use of odour absorbing and/or adsorbing components. Such substances are well known and may be incorporated into various compositions and packages according to the present invention e.g. zeolites, activated charcoals, etc.

[0047] Various compositions which may be used in various packages have been discussed. Their inclusion into packages may rely upon a variety of techniques.

[0048] For instance, according to one preferred aspect of the present invention the various components of the chosen system are incorporated into a bag or sachet. Typically this bag will be formed of a gas permeable but fluid impermeable material. This will allow gases, and usually water vapour, to pass through the walls of the bag as required. However they will prevent moisture, which is likely to be present in the package, from directly contacting the components of the bag or sachet. This will also help prevent contamination of the packaged articles by the components housed within the bag or sachet.

[0049] Micro-perforated films are one such material from which a bag may be constructed, or at least partly constructed. Other films and materials may also be relied upon and various apertures or vents to allow the required transfer of gases or vapours through the bag may be relied upon. The use of valv members may also be considered.

[0050] A modification is to use an oxygen absorbing

polymer for forming the sachet/container. These may provide sufficient oxygen absorbing properties for a typical package. Other parts of a package may be made from such materials. PCT patent application No. WO 94/12590 describes one such material.

[0051] As a variation of the bag, a rigid or semi-rigid container may be produced for insertion into a package. This may be substantially inflexible which may make it more difficult to disguise within a package. It could however, conceivably be moulded in a form disguising its presence. An example would be a substantially flat tray insert upon which the meat or articles were placed. Again various valve members, vents or variously permeable portions may be relied upon to allow the necessary flow of gas and vapours.

[0052] As a further variation of this concept the components could be housed within a compartment formed into the package or tray. The same options, variations and requirements as for the bag and rigid insert are also appropriate. However a disadvantage of a compartment in an actual package material (e.g. tray) is that for manufacturing simplicity and less problems for the end user, any of the required chemicals and substances are likely to be inserted into the compartment at the time of its manufacture. However it is generally appropriate that the required compositions are included at the time of packaging the meat or articles, depending upon the shelf life of the compositions.

[0053] The quantity of composition included is generally proportional to the quantity of meat or other articles to be packaged. Unless the weight and nature of the articles to be packaged are known, it is difficult to anticipate the correct amount of composition to include. Where discrete sachets or inserts are relied upon, one or more can be inserted, as appropriate, at the time of packaging. Alternatively the inclusion of one or more sachets or inserts could be relied upon to supplement the amount contained in any prefilled compartment. It is not generally desirable to have to load free chemicals or substances into a compartment while attempting to package meat or other articles, though automatic dispensers could be relied upon to insert appropriate amounts of compositions into packages or compartments.

[0054] Bags and sachets for containing various compositions may be formed individually though it is envisaged that strips or sheets of adjacent sachets may be manufactured. Typically the bags will be joined to each other but be separable by pulling or tearing. In some cases cutting may be relied upon though perforations facilitating tearing may be preferred in many instances.

[0055] Where the components of carbon dioxide evolving and oxygen removing systems are included in a single package, care must also be taken that the systems and components are compatible. In a preferred embodiment an 'organic acid with carb nate' type system is relied upon for carbon dioxide evolution. The term 'carbonate', as used to describe a component for CO_2 evolution, shall also include the 'hydrogen carbonates' (also known as bicarbonates). A common 'organic acid with carbonate' system of the present invention is citric acid with sodium hydrogen carbonat .

[0056] An iron (typically in the form of iron(II) sulphate) catalysed ascorbic acid system is relied upon for oxygen removal from the package. The ascorbic acid can also participate in carbon dioxide evolution, though as this is not its preferred role. The resulting ascorbate (from reaction with the carbonate) is still capable of oxygen removal. However, for economy, citric acid will often be the preferred acid for carbon dioxide evolution.

[0057] While a package according to the present invention may take a variety of forms, including a bag or container, it is envisaged that many retail ready embodiments of the present invention will comprise a tray with a covering film enabling the contents to be displayed in a shelf or refrigerator. The technology associated with such packaging is well known and may be relied upon in implementing such embodiments of the present invention. Technologies associated with other packaging forms which may be used with the present invention are also well known and could also be relied upon.

[0058] Modifications, for example to the package, may also be implemented. It has been mentioned previously that after packaging under carbon dioxide, meat will resume a reddish colour if re-exposed to oxygen. Accordingly, it will be necessary to introduce oxygen into the package to allow this reddening to occur. As most embodiments of the invention will have been packaged in a substantially oxygen free environment and with an oxygen impermeable covering, some means must be provided to allow oxygen to enter the package when required.

[0059] A physical opening could be created in the package, such as by the retailer breaching the integrity of the container or covering film (e.g. a knife cut, punched hole, etc.), though it is generally preferable that the package remains sealed. This leaves several possible options including the use of openable and closeable valve members to admit air. In other cases, vents which are normally closed may be revealed, perhaps by peeling off a cover layer. Other arrangements to provide a vent between the inside and outside of the package may be relied upon.

[0060] Another alternative is to rely upon the presence of an oxygen permeable film which will normally be covered during long term storage of the product under carbon dioxide. One method of use for such a film is to use an oxygen permeable film as a cover layer for the contents and to provide an oxygen impermeable layer overlying this. When it is desired to admit oxygen into the package, the covering barrier layer would be peeled or removed from the package. Such an arrangement need not only be applied as the main viewing window for the container but also in other positions on the package or tray.

[0061] A variety of highly permeable inner package

could be used in the masterpack concept. One particularly useful style is as follows:

1. Meat is placed in an appropriate tray for retail presentation.

2. It is then lidded with a prepunched permeable film, the punch holes being in appropriate positions so that they may be completely covered by a label or other seal at the point of sale. Alternatively lidded trays may be punched in situ on the lidding machine. Partial punch holes may also be formed so that no unwanted material contact the meat.

3. The individual trays of meat with the punched holes are stacked in a barrier bag within a carton. A sachet of the present invention is included.

4. The barrier bag is then evacuated in a chamber machine and gas flushed with sufficient Carbon dioxide to seal the carton.

[0062] At the point of sale the trays are removed allowing the ingress of oxygen through the punch holes. The trays are then sealed against leakage by the label or other sealant.

[0063] The punch holes allow the free circulation of gas which is necessary for efficient evacuation, gas flushing and eventual oxygenation. The labels or seals ensure a drip free container.

BRIEF DESCRIPTION OF DRAWINGS

[0064] Further aspects of the present invention will become apparent from the ensuing description which is given by way of example only and with reference to the accompanying drawings in which:

Figure 1 is a cross-sectional diagrammatic view of a bag embodiment of the present invention;

Figure 2 is a perspective diagrammatic view of a sheet-like array of bag embodiments such as illustrated in Figure 1;

Figure 3 is a cross-sectional diagrammatic view of a pellet-like embodiment of the present invention,

Figure 4 is a cross-sectional diagrammatic view of another embodiment of the present invention comprising a substantially solid insert;

Figure 5 is a cross-sectional diagrammatic view of an embodiment f the package according to the present invention;

Figure 6 is a cross-sectional diagrammatic view of a variation of figure 5;

Figure 7 is a cross-sectional diagrammatic view of a further variation of figure 5;

Figure 8 is a perspective diagrammatic view of an embodiment of a roll of detachable bags of Carbon dioxide evolving material;

Figure 9 is a further embodiment of the present invention, and

Figure 10 is a further embodiment of the present invention comprising a barrier bag with meat, and

Figure 11 is a diagrammatic view of a further embodiment of the present invention comprising an outer barrier bag, an internal permeable bag of meat products, and

Figure 12 is a further embodiment of the present invention, and

Figure 13 shows a number of packaged articles within an impermeable bag.

BEST MODES FOR CARRYING OUT THE INVENTION

[0065] By way of example and explanation several examples will now be given to illustrate various aspects of the present invention. These examples are not meant to be limiting nor are they meant to define the scope of the present invention.

Examples 1 - Carbon dioxide

[0066] In a preferred embodiment of the present invention the carbon dioxide evolving system comprises a solid acidic substance in combination with a substance reacting with said acid to release carbon dioxide. Typically the substance is a carbonate or hydrogen carbonate compound. Various mixtures of carbonates and/or hydrogen carbonates may be combined in various embodiments.

[0067] Typically, to prevent initiation of the carbon dioxide evolution process once the acid and carbonate (etc.) are mixed, all components should be solid. Accordingly, in many cases the acidic compound used will comprise an organic acid though other acidic compounds able to react with the carbonate (etc.) to release carbon dioxide are known and may be used.

[0068] In a preferred embodiment the carbon dioxide evolving system comprises citric acid in combination with sodium hydrogen carbonate. Each of these, providing they are of sufficient purity, ar commonly used food

additives and may be safely used in various embodiments of th present invention though other compounds may b used. Typically embodiments must comply with appropriate food contact legislation - this may place certain requirements on materials chosen for containing components and products of the Carbon dioxide evolving system; the outward passage of Carbon dioxide is required, though minimal leaching of other substances is desired.

[0069] Other carbon dioxide releasing chemical systems are known and may be incorporated in various embodiments of the present invention.

[0070] Systems in which carbon dioxide is initially adsorbed into a particular substance may also be relied upon, though subsequent release of the carbon dioxide may not always be at the rate or proportion desired. In contrast many systems such as the citric acid/hydrogen carbonate system previously described are more suitable for the more rapid initial release, followed by the trailing off, reaction profile desired for most embodiments. Combining the two types of system may be useful for customising a carbon dioxide release profile with respect to time.

[0071] Suitably containing the components of a reactive composition of the type dependent upon the presence of moisture, can be used as a control for the rate of reaction. The container could therefore be configured to govern moisture ingress. The container could also govern other means of initiation (e.g. heat, light, other electromagnetic radiation).

[0072] Such combinations may need to be stored in the presence of a drying agent until ready for use. Drying agents may be included to absorb small amounts of moisture which may come into contact with the components before their intended use.

[0073] The primary role of carbon dioxide generating is to replace that absorbed by articles within a package. Different package types and techniques may require different quantities of Carbon dioxide to be produced. For instance, a flexible pack which has been over-inflated with Carbon dioxide may only require the generation of a small amount of Carbon dioxide- perhaps 0.1 litre Carbon dioxide (STP) per kg of meat. On the other hand, for a rigid tray of a red meat, 1.0 litre or more of Carbon dioxide (STP) per kg of meat may be required.

Examples 2 - Oxygen Removal

[0074] A range of chemical and physical systems which can absorb, adsorb or otherwise remove oxygen are known. Each of these may be used in various embodiments of the present invention. Typically, for simplicity, the substances associated with the removal of oxygen from within the package will be combined with the carbon dioxide evolving substances. This requires some compatibility between the components and generally the simpler chemical or physical systems will be preferred.

[0075] In a preferred embodiment, th oxygen removal system relies upon ascorbic acid whose oxidisation by free oxygen in the package is catalysed by a small amount of iron compounds. The combination of such components with the citric acid/hydrogen carbonate system described under Example 1 appears compatible in tests to date. In a further preferred embodiment, sodium carbonate or bicarbonate and citric acid are combined with finely divided iron.

[0076] Other compounds and systems able to remove oxygen from a package are also known and documented in the art. These include the chemical oxidation of inorganic compounds (e.g. of sulphites, sulphur, hydrogen, metals, boron and silicon).

[0077] Other techniques rely upon the chemical oxidation of various organic compounds (including ascorbic acid) while others have relied on the oxidation of metals and metal coated plastics. Some systems have relied upon the replacement of oxygen by carbon dioxide.

[0078] Each of the foregoing methods may all be considered for use in the present invention. As most are known in the prior art, they will not be described further herein. In some cases the compatibility with carbon dioxide evolving systems may need to be investigated, or alternatively the oxygen removers separated from the carbon dioxide evolvers.

[0079] Where separation is called for, each particular system may be maintained in its own compartment or receptacle. However, rather than having separate receptacles to be added to a package, it is perhaps preferable that the different carbon dioxide evolving and oxygen removing systems are kept within their own compartments within a single sachet. This would allow the correct proportions of oxygen removing substances to carbon dioxide evolving substances to be pre-prepared. No matter how many sachets were added to a package, the correct proportions of each system would be maintained. In some cases maintaining these proportions may not be important other than for reasons of economy of materials.

Examples 3 - Sample Calculations

[0080] Take a thermoformed tray of thickness 500 microns and dimensions 25x10x5cm.

[0081] Volume of tray is 1250cc.

[0082] Surface area of tray is 0.06m^2.

[0083] If the tray is made from PVC, a typical Carbon dioxide transmission rate is 500cc per m^2 over 24 hours per 25 micron i.e. 500/20 per m^2 over 24 hours i.e. 25cc per m^2 in 24 hours.

[0084] The surface area of the tray is 0.06m^2 so we would expect to lose 1.5cc per day.

[0085] At 0°C permeation rate is reduced by a factor of approximately 4.2, therefore we would expect to lose 0.36cc per day through the tray.

[0086] Over the lifetime of the package i.e 10 weeks, the Carbon dioxide loss through the tray would b 25cc.

[0087] Th oxygen transmission rate of the PVC would be 150cc per m^2 over 24 hours per 25 micron, therefore the amount of oxygen entering the pack through the tray would b 7.5cc over ten weeks.

[0088] Typical transmission rates through the peelable barrier are as follows:

Carbon dioxide-25cc per m^2 24h
O_2- 5cc per m^2 24h

[0089] The surface area of the peelable barrier is $0.025m^2$.

[0090] At 0°C we would expect to lose 10cc of Carbon dioxide, through the peelable barrier, and allow the ingress of 2.0cc of oxygen.

[0091] Thus loss of Carbon dioxide would be limited to 35cc over the ten week lifetime of a package. This level could be easily replaced by a Carbon dioxide generator.

[0092] The total amount of oxygen permeating into the package over a ten week period would be approximately 9.5cc. This equates to 7,600 parts per million, which is high enough to induce spoilage of the product. (The maximum permissible oxygen level for Carbon dioxide packaging of beef is 500ppm, which is close to the level commonly achieved by vacuum/gas flushing machines). As a result, an oxygen remover would be required with a PVC tray.

[0093] If we assume that the meat occupies two thirds of the package, and that each kilo of meat requires at least 1.5 litres of Carbon dioxide, we would need to generate 1,240cc of Carbon dioxide. This could be generated by a sachet containing 4.65g of sodium bicarbonate, and 3.6g of citric acid.

Examples 4 - Containment of the Compositions

[0094] Compositions such as described in Examples 1 and 2 normally will be required to be contained in some manner.

Example 4A

[0095] Figure 1 illustrates one method of containing a composition 1. Here the composition 1 is contained within a bag or sachet 2 comprising two layers 3 of a flexible material sealed at the edges. Typically the flexible material 3 must be relatively highly permeable to carbon dioxide and oxygen. If the composition 1 is moisture activated then the film 3 must also allow the permeation of water vapour even though the film may be fluid impervious.

[0096] A variety of films having the desired characteristics are known though preferred are micro-perforated-films which provide high gas permeability but fluid impermeability. Vents and apertures may also be provided in films of different, types to provide the desired characteristics. Oxygen scavenging films may also be relied upon for construction of, and/or inclusion in, bags and sachets.

Example 4B

[0097] Figure 2 illustrates a sheet 4 of individual bags 2 which are separated by perforations 5. The perforations 5 allow individual bags or strips to be removed by pulling or tearing. These can then be used as required.

[0098] Figure 8 illustrates a roll 22 of sachets 2 which may be torn off for use.

Example 4C

[0099] Figure 3 illustrates a further embodiment of a composition according to the present invention. Here a pellet 6 comprising a compressed core 7 of composition is coated with a layer 8 of a suitable substance.

[0100] The coating 8 may be a dissolvable layer which gradually exposes the core for reaction. Many such compounds are known which would be suitable. However as the components of the composition will gradually be exposed, it would be desirable to place such an embodiment inside another receptacle, e.g. instead of the loose composition 1 as shown in Figure 1. In such an instance the coating layer 8 need not be provided if the compressed core 7 were housed within another receptacle.

[0101] As a variation a matrix comprising the desired components (for carbon dioxide generation/release and/or oxygen removal) in a dissolvable substitute may be provided. For instance a carbonate/organic acid/ascorbic acid system could be dispersed in a polyethylene oxide substrate (perhaps in a slurry using dichloromethane as a solvent) which is then formed or moulded to shape.

Example 4D

[0102] In Figure 4 is shown a further embodiment of the present invention where a composition 1 is provided in a rigid or semi-rigid container 9 which can be inserted into a tray. In Figure 4 is illustrated an embodiment where the insert 9 situated in the base portion of the tray and allows the meat or other articles to be placed on top.

[0103] The container 9 will generally be permeable to allow for at least the release of carbon dioxide and generally for the ingress of oxygen. The ingress of moisture may also be required in some instances. These features may be provided by forming the container of a suitably permeable material. Alternatively, strategically positioned vents or apertures may be relied upon, such as the base vents 10 illustrated in Figure 4. This type of embodiment could also rely upon the use of a valve member 11 which can be self operating or set to operate when the packag is filled.

Example 4E

[0104] Figure 5 illustrates an embodiment of the present invention in which a compartment 12 is formed into a tray 13. While the compartment may be semi-rigid, it may also comprise a layer of a suitably permeable film 14 adhering to the sides of the tray 13. Where the compartment is integrally formed, a window of a suitably permeable film may be provided. The general requirements of permeability which will allow the access and exit of components to and from the contained composition 1 have been previously discussed. Various methods of providing oxygen and carbon dioxide permeability have also been described.

[0105] The articles of meat 15 are also illustrated in Figure 5. An upper transparent cover 16 of an oxygen permeable material such as polyethylene is also shown. Covering this oxygen permeable layer 16 is a barrier layer 17 shown in a partially peeled position. After packaging, the oxygen barrier layer 17 totally covers and seals the permeable film 16. Immediately before display, where it is desired to return the red colour to meat, the barrier layer 17 is peeled back and removed from the package leaving a still sealed package in which the meat will reassume its red colour.

[0106] Figure 6 is a similar arrangement, though illustrates how the films 16, 17 can help retain the packaged meat in place i.e. the height of the meat is commensurate to the height of the tray - the film (16) contacts or comes into close proximity to the meat, thereby restricting its movement.

[0107] Figure 7 illustrates an alternative arrangement where the product is first packed using a highly oxygen permeable vacuum skin film. This package is then evacuated, gas flushed, and lidded with an oxygen barrier film. As a further variation on this theme, the product is overwrapped in a highly permeable film (by manual or mechanical means), then gas flushed and lidded with an oxygen barrier film. The sachet 2 may be included with the meat though in a preferred embodiment film 16 is sufficiently permeable for it to be placed within the intervening region (between film 16 and 17).

Examples 5 - Methods of Packaging

Example 5A

[0108] Two sirloin steaks weighing approximately 400g were vacuum skin packed to an amorphous PET tray using a highly permeable Intact film. The package was then evacuated, gas flushed with Carbon dioxide and sealed under a barrier lid. A perimeter seal only was applied.

[0109] The volume of the sealed tray was approximately 1.3 times the volume of the meat.

[0110] After 72 hours storage at 0°C the tray was highly distorted because most of the Carbon dioxide had been absorbed by the meat.

[0111] Two similar steaks to the previous example were vacuum skin packed to an identical tray. A sachet consisting of 4.5g of Sample Formulation A and 5cc of water was placed on top of th vacuum skin film. The tray was evacuated, gas flushed with Carbon dioxide, then sealed under a peelable barrier lid.

[0112] After 72 hours storage at 0°C no distortion of the tray was evident.

[0113] The lidding film could be removed from the tray without disturbing the highly permeable skin film, allowing the product to rebloom.

[0114] A very low volume package with a storage life of up to 12 weeks at -1°C had been produced using relatively low cost materials. The low volume of the package resulted in savings in packaging materials and distribution costs and a reduction in the amount of waste generated.

Example 5B

[0115] A special lidding film was prepared. This consisted of an adhesive layer (for adhesion to the tray) and a highly permeable polyethylene layer weakly bonded to an oxygen barrier layer.

[0116] Two sirloin steaks weighing approximately 400g were placed in an amorphous PET tray. The tray was evacuated , gas flushed with Carbon dioxide and sealed at the perimeter using the special lidding film.

[0117] After 72 hours storage at 0°C the tray was highly distorted.

[0118] Two similar steaks were packaged in an identical procedure, except that a sachet consisting of 4.5g of Sample Formulation A in a microporous film was included with the meat.

[0119] After 72 hours storage at 0°C no distortion of the tray was evident.

[0120] The barrier layer could be removed, leaving behind a highly permeable polyethylene layer. This allowed the meat to rebloom.

[0121] These very low volume packages could be stored for up to 12 weeks at -1°C. After reblooming they were ready for retail display.

Example 5c

[0122] Two sirloin steaks weighing approximately 400g were placed in a 500 micron PVC tray.

[0123] 4.5g of Sample Formulation A was placed in a sachet. One side of the sachet wall had attached a pressure sensitive adhesive layer. The sachet was adhered to the tray.

[0124] The tray was evacuated, gas flushed with Carbon dioxide and perimeter sealed simultaneously under two webs. The first web consisted of an antifog containing adhesive layer for PVC and a permeable layer. The second web consisted of a peel seal layer for the outer layer of the first web and a high barrier layer such as EVOH.

[0125] The packages had excellent storage lives as in the previous examples. The barrier layer could b removed at the point of sale allowing retail display in the bloomed stat .

[0126] The sachet could also be adhered to the lidding film.

[0127] In the preceding examples the sachets had enabled meats to be packed in high product to pack volume trays, under a low oxygen high carbon dioxide atmosphere. The atmosphere is highly conducive to a long storage and display life.

Example 5d

[0128] Eight legs of lamb weighing approximately 16kg wrapped in a moisture absorbent, gas permeable material were placed inside a foil pouch contained within a carton. The pouch was evacuated and then gas flushed, so that the carton could just be sealed (10L of Carbon dioxide). After prolonged chilled storage the carton was opened and it was found that the pouch clung tightly to the meat cuts, as all the Carbon dioxide had been absorbed by the meat. Inadequate Carbon dioxide had been added.

[0129] A similar package was prepared, except that the foil laminate pouch was gas flushed so that 24L of Carbon dioxide was used. The carton could not be sealed as the pouch was too large. After 24 hours chilled storage, the carton was retrieved from the storeroom and sealed, as sufficient amounts of Carbon dioxide had by then be absorbed. After prolonged chilled storage, the carton was opened and the pouch was found to be a loose fit, indicating that an adequate amount of Carbon dioxide had been added.

[0130] A larger case was used with the foregoing example where 24L of Carbon dioxide was used in the gas flushing stage. This could be sealed, but the larger volume meant that fewer cases could be packed into a container for shipping. After prolonged chilled storage the carton was opened and the pouch was still a loose fit, indicating that an adequate amount of Carbon dioxide had been added.

[0131] Similarly, eight legs of lamb were packed in a carton as in Example I. A moisture activated carbon dioxide release/oxygen absorber sachet was prepared by sealing 100g of Sample Formulation I into a microperforated film. The sachet was placed in the pouch which was evacuated and gas flushed with 10L of Carbon dioxide. The sachet generated 13.8L of Carbon dioxide and absorbed any oxygen remaining in the package. Low volume cartons had been used, and the cartons could be sealed immediately after the pouch had been sealed. After prolonged storage the pouch was found to be a loose fit indicating that sufficient gas had been added.

[0132] After one week the oxygen concentration was less than 10ppm and this level of oxygen was retained throughout the lifetime of the package.

[0133] A similar package was prepared except that a transparent barrier bag was used in place of th foil laminate bag. No difference in product quality was observed after prolonged periods of storage. The use of an oxygen absorber had allowed the expensive foil pouch to be replaced with a cheap r coextruded bag.

[0134] Cuts of lamb (total weight of 10 kg) wrapped in a highly permeable film or in highly permeable containers were also placed in a similar pouch, which was evacuated and gas flushed with 0.5L of Carbon dioxide per kg of meat (5L total). A sachet consisting of 95g of Sample Formulation H wrapped in a damp absorbent towel was added to the package. This was capable of generating 10L of Carbon dioxide and absorbing up to 2L of oxygen. The oxygen absorber removed residual oxygen introduced into the pouch by the retail ready packs. This allowed a masterpack of shelf ready cuts with a long storage life to be obtained. The oxygen concentration rapidly reduced to less than 10 parts per million and was retained at this level for the lifetime of the package.

[0135] Similar results were obtained with retail ready packs of beef steak.

Example 5e

[0136] Eight legs of lamb weighing approximately 16kg were wrapped in an absorbent material. A sachet containing 150g of Sample Formulation I in a microporous film was added.

[0137] The pouch was evacuated and sealed. No Carbon dioxide was added.

[0138] Within two days the package was a loose fit, indicating that an excess of Carbon dioxide had been generated.

[0139] The legs of lamb had a storage life of greater than 12 weeks at -1°C. This was much better than comparable vacuum packs.

[0140] The oxygen concentration was less than 10 parts per million throughout the lifetime of the package.

[0141] A simple vacuum packaging machine had been used to produce carbon dioxide gas enriched packages similar to those produced by the Captech process.

Example 5f

[0142] Eight legs of lamp wrapped in absorbent material were placed in a barrier pouch.

[0143] Excess air was displaced from the pouch and a sachet consisting of 128g of Sample Formulation G was added.

[0144] The pouch was heat sealed. No vacuum or gas flushing had been used.

[0145] After seven days the oxygen concentration in the package was less than 10 parts per million.

[0146] The storage life was equivalent to that described in the previous example.

[0147] No sophisticated or expensive equipment had

been used.

Examples 6

[0148] A number of sachets 2 wer prepared by sealing 3g of Sample Formulation C into a microporous film (dimensions approximately 35 x 35 mm).

[0149] The sachets were stored in the presence of silica gel.

[0150] With reference to Figure 9, a sirloin steak 15 weighing approximately 250g was placed in a 500 micron thick PET (polyethylene terephthalate) tray. The steak 15 was vacuum skin packaged using a highly permeable Trigon INTACT™ film 16. One sachet 2 was placed above the vacuum skin packaging film and 5cc of water was added. The tray was then evacuated, gas flushed with carbon dioxide and sealed under a peelable barrier film.

[0151] The packages were stored at -1.5°C for extended periods. No distortion of the packages occurred.

[0152] The peelable barrier film 17 and the sachet 2 could both be removed at the same time allowing the meat to rebloom. To the consumer, the product would appear as a bright red steak on a tray overwrapped with skin film. This embodiment would be useful for where consumer resistance to the presence of a sachet is a problem.

[0153] Like the previous examples a drip absorption system could be used to enhance package appearance.

[0154] At various intervals samples were removed from storage and compared to identical vacuum packaged steaks. These were packed at the same time using a pouch of similar permeability to the PET tray/barrier film combination used in this example. Meat packed using the system of example 6 had markedly lower bacteria counts than the vacuum packed steaks and a longer storage life. The colour in the oxygenated state was much better than for the vacuum packed steaks. The meat could be packed at a processing plant and supplied direct to retail outlets, where it could be displayed in its oxygenated state without repacking.

Example 7

[0155] Some formulations suitable for use as carbon dioxide generators and oxygen removers are as follows. These formulations may be broken down into smaller quantities for use according to the present invention. It is envisaged that for many examples the chemical systems will be present in sachets or inserts for inclusion into a package.

A	Sodium bicarbonate	450g
	Fumaric acid	288g
	$FeCl_2.4H_20$	40g
	Sodium ascorbate	210g
B	Sodium carbonate	283g
	Sodium bicarbonate	225g
	Fumaric acid	288g
	$FeCl_2.4H_20$	40g
	Sodium ascorbate	210g
C	Sodium bicarbonate	450g
	Citric acid	311g
	Ascorbic acid	60g
	$FeCl_2.4H_20$	3g
D	Sodium bicarbonate	150g
	Citric acid	51g
	EDTA	10g
	Ascorbic acid	50g
	$FeCl_2.4H_20$	5g
E	Sodium bicarbonate	180g
	EDTA	150g
	$FeCl_2.4H_20$	50g
F	Sodium bicarbonate	130g
	Poly(acrylic acid)	100g
	$FeCl_2.4H_20$	50g
G	Sodium bicarbonate	133g
	Citric acid	102g
	Iron powder	20g
H	Sodium bicarbonate	450g
	Fumaric acid	288g
	$FeCl_2.4H_20$	100g
	Sodium ascorbate	210g
I	Sodium bicarbonate	450g
	Fumaric acid	288g
	Sodium ascorbate	53g
	$FeSO_4.H_2O$	10g

(continued)

J	Sodium bicarbonate	450g
	Fumaric acid	288g
	Sodium ascorbate	355g
	$FeCl_2.4H_2O$	40g

Examples 8

[0156] As a further variation Figures 10 and 11 illustrate alternative embodiments of the present invention. Figure 10 illustrates a barrier outer bag containing meat product and inserts containing a carbon dioxide generating and oxygen removing substance. Preferably the included materials are able to generate carbon dioxide independently of oxygen removal and have sufficient capacity to produce at least two times as much carbon dioxide gas (measured as a molar ratio) as the ability for oxygen removal. More preferably this ratio is 5:1 or higher. The quantity of included material should also be sufficient to ensure that there is at least the ability to generate at 0.1 litres or more of carbon dioxide (measured at STP) per kilogram of enclosed meat. The meat product may be wrapped in a material known as absorber pad. A material known as "Absorba Pad" is a laminate of perforated plastics and an absorber material such as paper.

[0157] In Figure 11 is illustrated an alternative embodiment in which the meat is packaged within an internal permeable bag. The inner bag should be permeable to both carbon dioxide and oxygen. The outer bag remains as a barrier material and ideally the carbon dioxide generating and oxygen removing material is positioned between the two bag layers.

[0158] With respect to Figure 12, an insert 2 within a tray 13 containing meat 15 is lidded by two layers of film 18, 19, layer 18 being a barrier layer and layer 19 being a permeable layer.

[0159] Figure 13 illustrates a number of packages 20 within a impermeable container 21. The interior of the container may be gas flushed or evacuated after loading. Packages 20 may come in many forms. For example the package may be a filled bag, it may be a skin-to-skin package, it may be a lidded tray where the tray is permeable, or any other form of composite pack.

[0160] The packages described by way of example are characterised by the fact that there is minimal air or head space, the packaging process can be completed in one step and where trays are used tray distortion is not a problem.

[0161] Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

Claims

1. A method of packaging meat or other foodstuffs in a carbon dioxide rich, low oxygen package environment comprising

   providing a food package of a gas barrier material,
   placing a food product within said food package,
   placing in said package with said food product a carbon dioxide generating material and an oxygen removing material, and
   sealing said package,
   said carbon dioxide material generating carbon dioxide in a volume not dependent upon the removal of oxygen and greater than twice the mole ratio of oxygen removed by said oxygen removing material.

2. A method according to Claim 1 wherein said package is evacuated prior to sealing to provide a reduced volume of air in said package when sealed.

3. A method according to Claim 1 wherein said package is gas flushed before sealing to provide a modified atmosphere in said package when sealed.

4. A method according to Claim 3 wherein said package is gas flushed with carbon dioxide prior to sealing to provide an atmosphere therein having a carbon dioxide content higher than the carbon dioxide content of air.

5. A method of packaging meat or other foodstuffs in a carbon dioxide rich, low oxygen package environment comprising

   providing a food package including an outer enclosure of a gas barrier material and an interior member of a gas permeable material dividing the outer enclosure into two interior spaces,
   placing a food product in one of said interior spaces within said outer enclosure,
   placing a carbon dioxide generating material and an oxygen removing material in the other of said interior spaces within said outer enclosure such that said gas permeable member is between the food product and said carbon dioxide generating material and said oxygen removing material, and
   sealing said outer enclosure,
   said carbon dioxide generating material generating carbon dioxide, over time, in a volume not dependent upon the removal of oxygen and greater than twice the mole ratio of oxygen removed by said oxygen removing material.

6. A method according to claim 5 wherein the rate and volume of carbon dioxide generated is predetermined and proportional to the mass of the food product within said packag .

7. A food package for meat or other foodstuffs (15) comprising

   a sealed enclosure (13, 17, 18) of a gas barrier material
   a food product (15) confined in said enclosure, and
   a carbon dioxide generating material and an oxygen removing material (1, 7) also confined in said enclosure, said carbon dioxide generating material and said oxygen removing material being capable, over time, of removing oxygen from the atmosphere within said enclosure to provide a low oxygen environment therein and of generating carbon dioxide in a volume not dependent upon the removal of oxygen characterised in that the volume of carbon dioxide generated is greater than twice the mole ratio of oxygen removed to provide a carbon dioxide rich environment within said enclosure.

8. A food package according to claim 7 wherein said carbon dioxide generating and oxygen removing materials (1) are confined in a permeable packet or sachet (2).

9. A food package according to claim 7 or 8 including a gas permeable member (14) dividing said enclosure into two internal spaces and wherein the food product is confined in one of said spaces and said carbon dioxide generating and oxygen removing materials (1) are confined in the other of said spaces.

10. A food package according to claim 9 wherein said enclosure comprises a bag of gas barrier material.

11. A food package according to claim 9 or 10 wherein said gas permeable member comprises a sealed bag (16) in which the food product (15) is confined.

12. A food package according to claim 9 wherein said enclosure comprise a tray (13) having a bottom and sides defining an interior space with an open top and a closure member (16,17) across the top of said tray and sealed to said tray, and wherein said gas permeable member is a film layer (14) beneath and generally coextensive with said closure member (18).

13. A food package according t claim 7, 8 or 9 wherein said enclosure comprises a tray (13) having an open top and bottom and side walls defining an interior space, and a gas barrier film layer (17, 18) closing th open top of said tray.

14. A food package according to claim 9 or claims 9 and 13 wherein said gas permeabl member comprises a film layer (14) generally coextensive with said gas barrier film layer (17) but spaced therefrom.

15. A food package according to any of claim 7 to 14 wherein said carbon dioxide generating material is capable of generating carbon dioxide at a rate and of a volume in a predetermined proportion to the mass of the food product (15) in said enclosure.

16. A food package according to claim 15 wherein said carbon dioxide generating material is capable of generating carbon dioxide at a rate and of a volume sufficient for absorption of carbon dioxide by the food product (15) and to maintain a desired internal pressure within said enclosure.

17. A food package according to claim 16 wherein said carbon dioxide generating material is capable of generating one litre of carbon dioxide per kilogram of the food product (15).

Patentansprüche

1. Verfahren zum Verpacken von Fleisch oder anderen Nahrungsmitteln in eine

   Verpackungsumgebung, die an Kohlendioxid reich ist, mit geringem Sauerstoff, das umfasst, eine Nahrungsmittelverpackung von einem Gasbarrierenmaterial zu liefern,
   ein Nahrungsmittelprodukt in die Nahrungsmittelverpackung zu bringen,
   in die Verpackung mit dem Nahrungsmittelprodukt ein Kohlendioxiderzeugungsmaterial und ein Sauerstoffentfernungsmaterial zu bringen, und
   die Verpackung abzudichten,
   wobei das Kohlendioxidmaterial Kohlendioxid mit einem Volumen erzeugt, das nicht von der Entfernung von Sauerstoff abhängt und größer als zweimal des Molverhältnisses von dem Sauerstoff ist, der von dem Sauerstoffentfernungsmaterial entfernt wird.

2. Verfahren nach Anspruch 1, in dem die Verpackung vor dem Abdichten evakuiert wird, um ein verringertes Luftvolumen in der Verpackung zu liefern, wenn sie abgedichtet ist.

3. Verfahren nach Anspruch 1, in dem die Verpackung mit Gas gespült wird, bevor si abgedichtet wird, um eine modifizierte Atmosphäre in der Verpak-

kung zu liefern, wenn sie abgedichtet ist.

4. Verfahren nach Anspruch 3, in dem die Verpackung mit Kohlendioxidgas gespült wird, bevor sie abgedichtet wird, um eine Atmosphäre darin mit einem Kohlendioxidgehalt zu liefern, der höher als der Kohlendioxidgehalt von Luft ist.

5. Verfahren zum Verpacken von Fleisch oder anderen Nahrungsmitteln in eine Verpackungsumgebung, die an Kohldioxid reich ist, mit geringem Sauerstoff, das umfasst, eine Nahrungsmittelverpackung einschließlich einer äußeren Umschließung eines Gasbarrierenmaterials und eines inneren Glieds aus einem gasdurchlässigen Material zu liefern, das die äußere Umschließung in zwei innere Räume aufteilt,

   ein Nahrungsmittelprodukt in einen der inneren Räume innerhalb der äußeren Umschließung zu bringen,
   ein Kohlendioxiderzeugungsmaterial und ein Sauerstoffentfernungsmaterial in den anderen der inneren Räume in der äußeren Umschließung zu bringen, so dass das gasdurchlässige Glied zwischen dem Nahrungsmittelprodukt und dem Kohlendioxiderzeugungsmaterial und dem Sauerstoffentfernungsmaterial ist, und
   die äußere Umschließung abzudichten,
   wobei das Kohlendioxiderzeugungsmaterial über eine Zeitdauer Kohlendioxid mit einem Volumen erzeugt, das nicht von der Entfernung von Sauerstoff abhängt und größer als zweimal des Molverhältnisses von Sauerstoff ist, der von dem Sauerstoffentfernungsmaterial entfernt wird.

6. Verfahren nach Anspruch 5, in dem die Geschwindigkeit und das Volumen von erzeugtem Kohlendioxid vorbestimmt ist und proportional zu der Masse des Nahrungsmittelprodukts in der Verpackung ist.

7. Nahrungsmittelverpackung für Fleisch oder andere Nahrungsmittel (15), die folgendes umfasst

   eine abgedichtete Umschließung (13, 17, 18) aus einem Gasbarrierenmaterial,
   ein in der Umschließung eingesclossenes Nahrungsmittelprodukt, und
   ein Kohlendioxiderzeugungsmaterial und ein Sauerstoffentfernungsmaterial (1,7), die auch in der Umschließung eingeschlossen sind, wobei das Kohlendioxiderzeugungsmaterial und das Sauerstoffentfernungsmaterial über eine Zeitdauer Sauerstoff von der Atmosphäre innerhalb der Umschließung entfernen können, um eine Umgebung mit geringem Sauerstoff darin zu liefern, und Kohlendioxid mit einem Volumen zu erzeugen, das nicht von der Entfernung von Sauerstoff abhängt, dadurch gekennzeichnet, dass das Volumen des erzeugten Kohlendioxids größer als zweimal des Molverhältnisses des entfernten Sauerstoffs ist, um eine kohlendioxidreiche Umgebung in der Umschließung zu liefern.

8. Nahrungsmittelverpackung nach Anspruch 7, in der Kohlendioxiderzeugungs- und Sauerstoffentfernungsmaterialien (1) in einem durchlässigen Päckchen oder Kissen (2) eingeschlossen sind.

9. Nahrungsmittelverpackung nach Anspruch 7 oder 8, die ein gasdurchlässiges Glied (14) einschließt, das die Umschließung in zwei innere Räume aufteilt, und in der das Nahrungsmittelprodukt in einem der Räume eingeschlossen ist und die Kohlendioxiderzeugungs- und Sauerstoffentfernungsmaterialien (1) in dem anderen der Räume eingeschlossen sind.

10. Nahrungsmittelverpackung nach Anspruch 9, in der die Umschließung einen Beutel aus Gasbarrierenmaterial umfasst.

11. Nahrungsmittelverpackung nach Anspruch 9 der 10, in der das gasdurchlässige Glied einen abgedichteten Beutel (16) umfasst, in dem das Nahrungsmittelprodukt eingeschlossen ist.

12. Nahrungsmittelverpackung nach Anspruch 9, in der die Umschließung ein Schale (13) mit einem Boden und Seiten umfasst, die einen inneren Raum mit einem offenen Oberteil definieren, und ein Schließglied (16,17) über dem Oberteil der Schale, und das an der Schale abgedichtet ist, und in der das gasdurchlässige Glied eine Folienschicht (14) unter dem Schließglied (18) ist, und das sich damit im allgemeinen erstreckt.

13. Nahrungsmittelverpackung nach Anspruch 7, 8 oder 9, in der die Umschließung eine Schale (13) mit einem offenen Oberteil und einem Boden und Seitenwänden umfasst, die einen inneren Raum definieren, und eine Gasbarrierenfolienschicht (17, 18), die das offene Oberteil der Schale schließt.

14. Nahrungsmittelverpackung nach Anspruch 9 oder Ansprüchen 9 und 13, in der das gasdurchlässige Glied eine Folienschicht (14) umfasst, die sich im allgemeinen mit der Gasbarrierenfolienschicht erstreckt (17), aber davon beabstandet ist.

15. Nahrungsmittelverpackung nach einem der Ansprüche 7 bis 14, in der das Kohlendioxiderzeugungsmaterial Kohlendioxid mit einer Geschwindigkeit und mit ein m Volumen in einem

vorbestimmten Verhältnis zu der Masse des Nahrungsmittelprodukts (15) in der Umschließung erzeugen kann.

16. Nahrungsmittelverpackung nach Anspruch 15, in der das Kohlendioxiderzeugungsmaterial Kohlendioxid mit einer Geschwindigkeit und mit einem Volumen erzeugen kann, das für die Absorption von Kohlendioxid von dem Nahrungsmittelprodukt (15) und zum Halten eines erwünschten inneren Drucks in der Umschließung ausreicht.

17. Nahrungsmittelverpackung nach Anspruch 16, in der das Kohlendioxiderzeugungsmaterial einen Liter Kohlendioxid pro Kilogramm des Nahrungsmittelprodukts (15) erzeugen kann.

Revendications

1. Méthode de conditionnement de viande ou autres produits alimentaires en environnement riche en dioxyde de carbone et pauvre en oxygène comportant:

   l'apport d'un matériau servant de barrière au gaz à un conditionnement alimentaire,
   la mise d'un produit alimentaire dans ledit conditionnement alimentaire,
   la mise dans ledit conditionnement avec ledit produit alimentaire d'un matériau générateur de dioxyde de carbone et d'un matériau éliminateur d'oxygène, et
   la fermeture hermétique dudit conditionnement,
   ledit matériau générateur de dioxyde de carbone dégageant le dioxyde de carbone en volume indépendant de l'élimination de l'oxygène et deux fois supérieur au rapport molaire éliminé par ledit matériau éliminateur d'oxygène.

2. Méthode selon la revendication 1 suivant laquelle ledit conditionnement est évacué avant la fermeture hermétique de manière à assurer une volume réduit d'air dans ledit conditionnement suite à sa fermeture hermétique.

3. Méthode selon la revendication 1 suivant laquelle ledit conditionnement est purgé avec un faisceau de gaz avant d'effectuer la fermeture de manière à assurer une atmosphère modifiée dans ledit conditionnement lorsque ledit conditionnement a l'objet d'une fermeture hermétique.

4. Méthode selon la revendication 3 suivant laquelle ledit conditionnement est purgé avec un faisceau de dioxyde de carbone avant la fermeture de manière à y assurer une atmosphère d nt la teneur en dioxyde de carbone est supérieure à la teneur de l'air en dioxyde de carbon .

5. Méthode selon de conditionnement de la viande ou d'autres produits alimentaires en environnement riche en dioxyde de carbone et pauvre en oxygène comportant:

   la formation d'un conditionnement prévoyant un enclos extérieur de matériau barrière au gaz et un élément intérieur de matériau perméable au gaz séparant l'enclos extérieur en deux volumes intérieurs,
   la mise d'un produit alimentaire dans l'un desdits volumes dans l'enclos extérieur,
   la mise d'un matériau générateur de dioxyde de carbone et d'un matériau éliminateur d'oxygène dans l'autre desdits volumes intérieurs dans ledit enclos extérieur de façon telle que ledit élément perméable au gaz se trouve entre le produit alimentaire et ledit matériau générateur de dioxyde de carbone et ledit matériau éliminateur d'oxygène, et
   la fermeture hermétique dudit enclos extérieur, le dégagement dans le temps de dioxyde de carbone par le matériau générateur de dioxyde de carbone indépendamment de l'élimination de l'oxygène et deux fois supérieur au rapport molaire de l'oxygène éliminé par le matériau éliminateur d'oxygène.

6. Méthode selon la revendication 5 suivant laquelle le taux et le volume de dioxyde de carbone dégagé est prédéterminé et proportionnel à la masse de produit alimentaire dans ledit conditionnement.

7. Conditionnement alimentaire pour la viande ou d'autres produits alimentaires (15) comportant:

   un enclos fermé hermétique (13,17,18) en matériau formant barrière au gaz
   un produit alimentaire (15) retenu dans ledit enclos, et
   un matériau générateur de dioxyde de carbone et un matériau éliminateur d'oxygène (1, 7) également retenu dans ledit enclos, ledit matériau générateur de dioxyde de carbone et le matériau éliminateur d'oxygène étant susceptibles dans le temps d'éliminer l'oxygène de l'atmosphère dudit enclos pour y assurer un environnement faible en oxygène et de dégager le dioxyde de carbone en volume indépendant de l'élimination de l'oxygène caractérisé en ce que le volume de dioxyde de carbone dégagé est deux fois supérieur au rapport molaire de l'oxygène éliminé pour assurer un environnement riche en dioxyde de carbone dans ledit enclos.

8. Conditionnement alimentaire selon la revendication 7 suivant laquelle les matériaux générateur de dioxyde de carbone et éliminateur d'oxygène (1) sont retenus dans un paquet ou sachet perméable (2).

9. Conditionnement alimentaire selon la revendication 7 ou 8 contenant un élément perméable au gaz (14) séparant ledit enclos en deux volumes intérieurs et dans lesquels le produit alimentaire est retenu dans l'un desdits volumes et lesdits matériaux générateur de dioxyde de carbone et éliminateur d'oxygène (1) sont retenus dans l'autre desdits volumes.

10. Conditionnement alimentaire selon la revendication 9 dont ledit enclos comporte un sac en matériau formant barrière au gaz.

11. Conditionnement alimentaire selon la revendication 9 ou 10 dont ledit élément perméable au gaz comporte un sac à fermeture hermétique (16) dans lequel le produit alimentaire (15) est retenu.

12. Conditionnement alimentaire selon la revendication 9 dont ledit enclos comporte un plateau (13) ayant un fond et des côtés définissant un vide intérieur ouvert en partie supérieure avec un élément de fermeture (16, 17) en travers du niveau supérieur dudit plateau et fermé hermétique sur ledit plateau, et dont l'élément perméable au gaz est une couche de feuillard (14) située sous et généralement coextensive avec ledit élément de fermeture (18).

13. Conditionnement alimentaire selon les revendications 7, 8 ou 9 dont ledit enclos comporte un plateau (13) ayant un niveau supérieur ouvert et des parois inférieure et latérales définissant un vide intérieur, et une couche de feuillard formant barrière au gaz (17, 18) fermant le niveau supérieur ouvert dudit plateau

14. Conditionnement alimentaire selon la revendication 9 ou les revendications 9 et 13 dont ledit élément perméable au gaz comporte une couche de feuillard (14) généralement en coextensive avec ladite couche de feuillard formant barrière au gaz (17) mais située espacée.

15. Conditionnement alimentaire selon l'une ou l'autre des revendications 7 à 14 dont ledit matériau générateur de dioxyde de carbone est en mesure de dégager le dioxyde de carbone selon un taux et un volume en proportion prédéterminée par rapport à la masse de produit alimentaire (15) dans ledit enclos.

16. Conditionnement alimentaire selon la revendication 15 dont ledit matériau générateur de dioxyde de carbone est en mesure d dégager le dioxyde de carbone selon un taux et en volume suffisant à l'absorption du dioxyde de carbone par le produit alimentaire (15) et de maintenir la pression intérieure recherchée dans ledit enclos.

17. Conditionnement alimentaire selon la revendication 16 dont ledit matériau générateur de dioxyde de carbone est en mesure de dégager un litre de dioxyde de carbone par kilogramme de produit alimentaire (15).

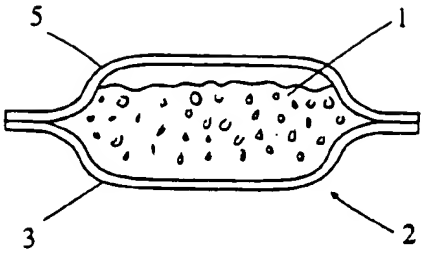

FIG. 1.

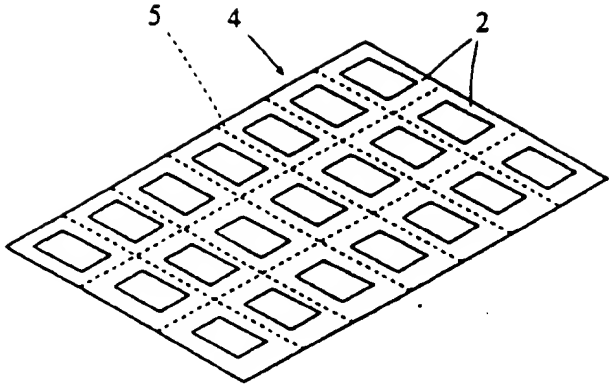

FIG. 2.

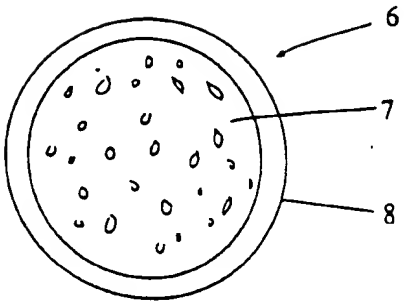

FIG. 3.

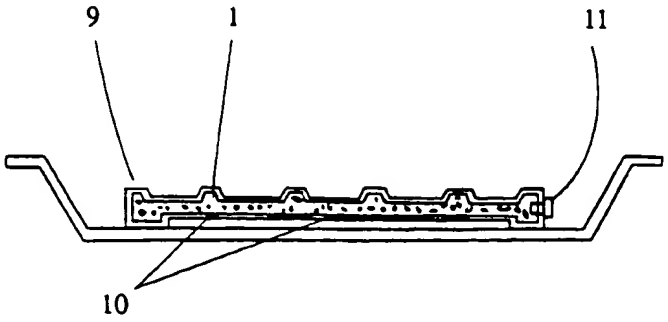

FIG. 4.

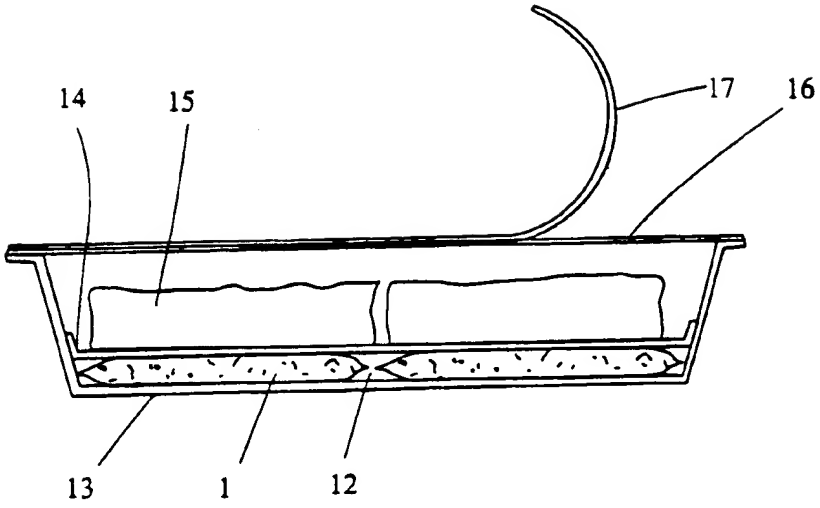

FIG. 5.

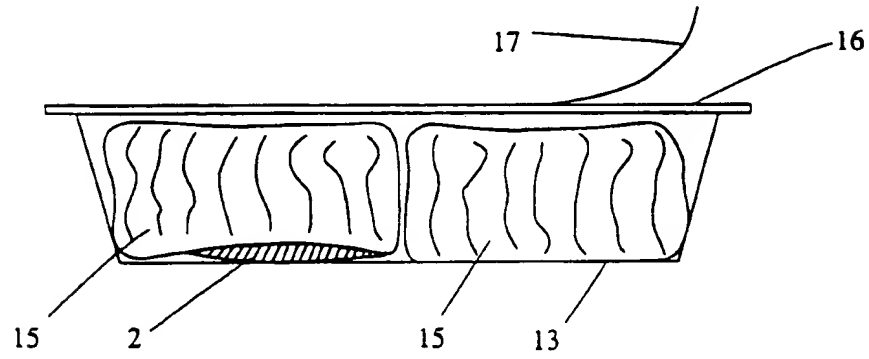

FIG. 6.

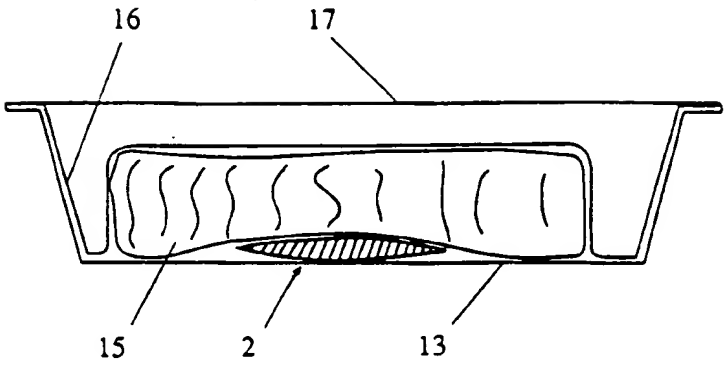

FIG. 7.

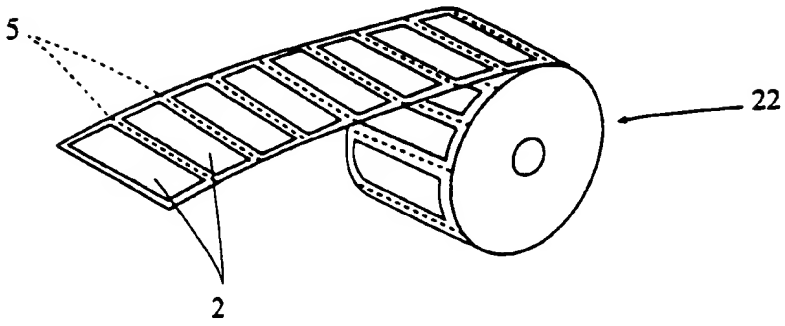

FIG. 8

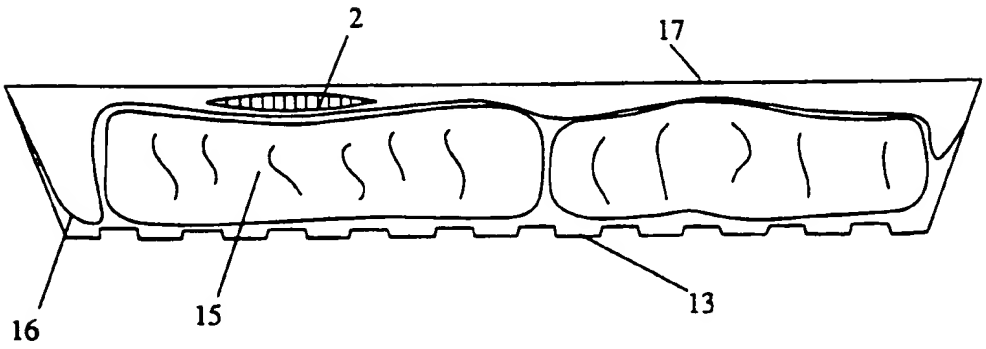

FIG. 9

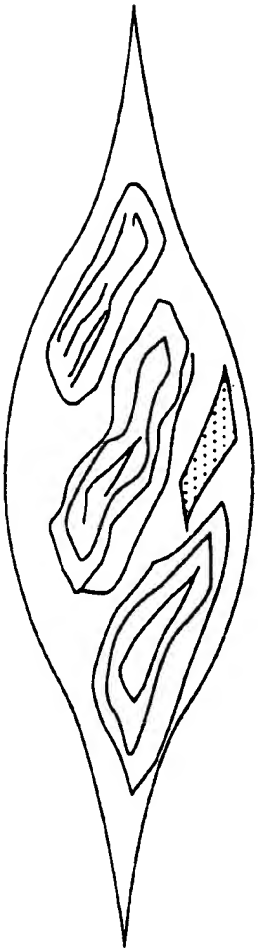

FIG. 10

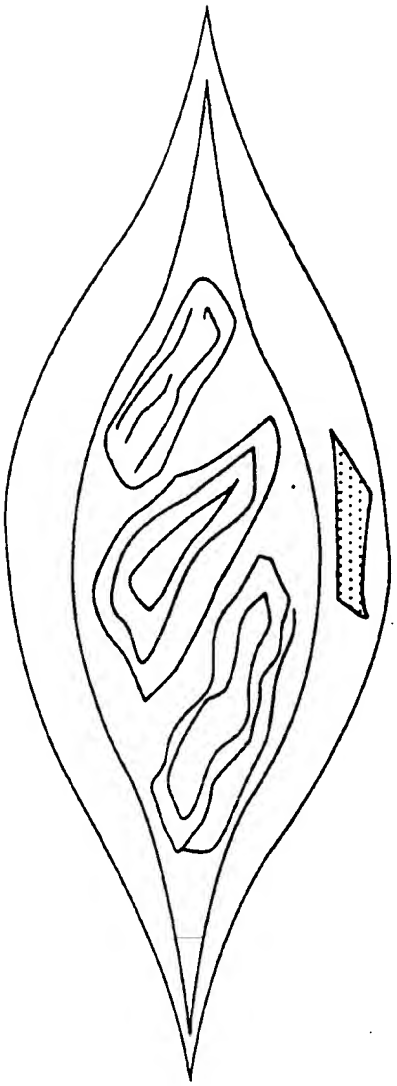

FIG. 11

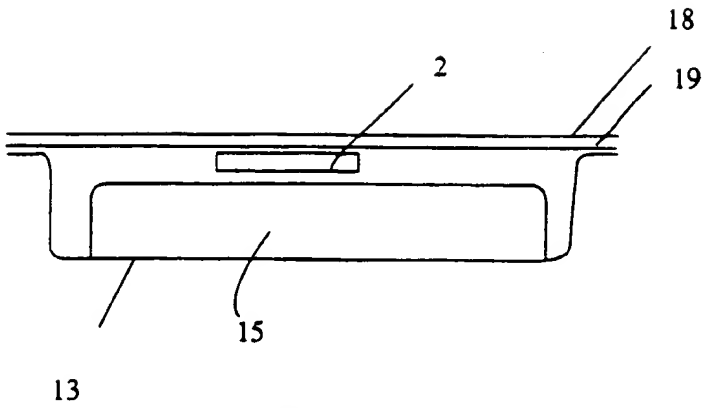

FIG. 12

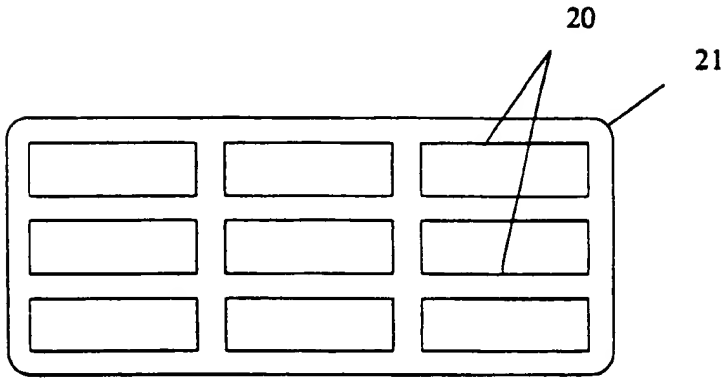

FIG. 13

DERWENT-ACC-NO: 1970-05519R
DERWENT-WEEK: 197004

TITLE: Preserving natural colour of foodstuffs by treatment - with gases

PATENT-ASSIGNEE: VERBRUGGEN MARIA LOUISA [VER I]

PRIORITY-DATA:
1968BE-0061137 July 18, 1968

PATENT-FAMILY:

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BASIC-ABSTRACT:
The natural colour of foodstuffs such as meat meat products, blood, fish is preserved by treating with a gas such as carbon monoxide either on the pure state or containing a reducing agent such as SO2, H and NO, also a neutral gas such as N2 or CO2. Before the gas treatment the foodstuff is subjected to vacuum treatment. Illuminatin g gas is used for treatment.

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(54) Bezeichnung: Verfahren zur Erteilung oder Konservierung einer natürlichen Färbung von Nahrungsmitteln

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Verfahren zur Erteilung oder Konservierung einer natürlichen Färbung von Nahrungsmitteln

- - -

Die Erfindung betrifft ein Verfahren, mit dem Nahrungsmitteln wie beispielsweise Fleisch, Fleischprodukten, Blut, Fisch u. dgl. eine natürliche Färbung gegeben wird oder die natürliche Verfärburg konserviert wird. Die behandelten Nahrungsmittel können dabei in frischem Zustand, ggf. nach einer Kühlung verzehrt werden, sie können auch eingefroren oder getrocknet werden oder zur Herstellung von Konserven oder Halbkonserven benutzt werden.

Die bislang bekannten Verfahren dieser Art bestehen darin, die Nahrungsmittel, insbesondere Fleisch und Fleischprodukte, mit einer flüssigen Lösung von Sulfiten oder Nitriten zu behandeln. Nachteilig ist bei den vorbekannten Verfahren, daß zur Erzielung eines guten Ergebnisses die Konzentration der Sulfite oder Nitrite in der Lösung relativ hoch sein muß. Es besteht damit die Gefahr, daß freie Sulfite oder Nitrite in dem Fleisch oder dem Fleischprodukt verbleiben und dann beim späteren Verzehr einen schädlichen Einfluß auf den menschlichen Organismus ausüben. Darüber hinaus erfordern die bislang bekannten Verfahren eine große Verfahrensdauer.

Der vorliegenden Erfindung liegt die Aufgabe zugrunde, unter Beseitigung der vorstehend genannten Nachteile ein Verfahren zu schaffen, das sich einfach und schnell durchführen läßt, gute Ergebnisse bringt und eine Schädigung des menschlichen

Organismusses ausschließt. Die erfindungsgemäße Lösung besteht im wesentlichen darin, daß die Nahrungsmittel mit einem Gas behandelt werden, das Kohlenoxyd enthält.

Gemäß einer vorteilhaften Ausführungsform der Erfindung werden die Nahrungsmittel mit einem Gas behandelt, das ein Reduktionsgas enthält, das aus der von Schwefelsäureanhydrid, Wasserstoff und Stickstoffoxyd gebildeten Gruppe ausgewählt wird.

Gemäß einer weiteren vorteilhaften Ausführungsform der Erfindung wird ein Gas verwendet, das ein neutrales Gas enthält.

Gemäß einer besonders vorteilhaften Ausführungsform der Erfindung wird die Behandlung der Nahrungsmittel mit dem vorgenannten Gas vorgenommen, nachdem zuvor die Nahrungsmittel einer Vakuumbehandlung unterzogen wurden.

Das erfindungsgemäße Verfahren ist einfach und billig durchzuführen, es zeitigt gute Ergebnisse, benötigt keine übermäßig lange Zeit und vor allen Dingen sind die so behandelten Nahrungsmittel ohne jeden schädlichen Einfluß für den menschlichen Organismus.

Besonderheiten der Erfindung ergeben sich aus der nachfolgenden Beschreibung einer Ausführungsform der Erfindung.

Das erfindungsgemäße Verfahren besteht im wesentlichen darin, auf Nahrungsmittel, insbesondere Fleisch und Fleischprodukte, für eine ausreichend lange Zeitdauer ein Gas einwirken zu lassen, das Kohlenoxyd enthält.

Das Kohlenoxyd kann in reinem Zustand oder als Gemisch mit Reduktionsgasen wie beispielsweise Schwefelsäureanhydrid, Wasserstoff, Stickstoffoxyd, und/oder mit neutralen Gasen, wie beispielsweise Stickstoff und Kohlensäureanhydrid eingesetzt werden. Diese neutralen Gase können eingesetzt werden, um die Gefahr einer Gasentzündung herabzusetzen, oder um ihre neutralen Eigenschaften auszunutzen. Als Quelle für das Kohlenoxyd wird vorzugsweise Leuchtgas benutzt, das eine ausreichende Konzentration an Kohlenoxyd aufweist.

Das erfindungsgemäße Verfahren stützt sich zum Teil auf die die Färbung begünstigenden Eigenschaften der genannten Gase, zum Teil auf die bakteriziden Eigenschaften der Gase, zur Hauptsache jedoch auf die Eigenschaft des gasförmigen Kohlenoxydes, eine komplexe Verbindung mit dem Bestandteil Häm des Hämoglobins oder des Myoglobins einzugehen. Es bilden sich somit Verbindungen, deren Eigenschaften im Hinblick auf die Färbung des Produktes sehr wesentlich sind, unter anderem, weil die Farbe dieser Verbindungen sich stark der Farbe der Verbindungen annähert, die dem Fleisch, dem Fisch und so weiter die natürliche Farbe geben. Die auf diese Weise erreichte Färbung ist desweiteren sehr viel stabiler als die natürliche Färbung und verbleibt sehr viel besser in dem Produkt bei dessen Konservierung und weiteren Behandlung. So ist beispielsweise die Affinität des Kohlenoxydes für die Häme 200 mal größer als die des Sauerstoffes.

Um eine in die Tiefe gehende Behandlung mit Kohlenoxyd oder dem gasförmigen Kohlenoxydgemisch zu gewährleisten, und um eine solche Tiefenbehandlung schnell durchführen zu können, unterwirft man die Nahrungsmittel zuvor einer Vakuumbehandlung, nach der dann das Gas oder Gasgemisch auf der Basis Kohlenoxyd in Berührung mit den Nahrungsmitteln gebracht wird. Die Länge des Kontaktzeitraumes richtet sich dabei nach der Art und der Bearbeitungsweise der Nahrungsmittel. Werden die Nahrungsmittel dann an die normale Atmosphäre zurückgebracht, entweichen sämtliche freien Gase in die Atmosphäre, so daß die erfindungsgemäße Behandlung keinerlei merkbare Spuren hinterläßt.

Das erfindungsgemäße Verfahren hat somit bezüglich den bislang bekannten Naßbehandlungsverfahren den Vorteil, daß die überschüssigen Gase, die nicht mit dem Nahrungsmittel reagieren, automatisch durch Auslüftung aus den letzteren entfernt werden.

Ein weiterer Vorteil des Verfahrens besteht darin, daß es während der sonstigen Zubereitung und Konservierung der Nahrungsmittel durchgeführt werden kann.

Es versteht sich, daß im Rahmen des Erfindungsgedankens zahlreiche Abänderungen der oben beschriebenen konkreten Ausführungsform des Verfahrens möglich sind.

Patentansprüche

1. Verfahren zur Erteilung oder Konservierung einer natürlichen Färbung von Nahrungsmitteln, wie beispielsweise Fleisch, Fleischprodukten, Blut, Fisch u. dgl., dadurch gekennzeichnet, daß die Nahrungsmittel mit einem Gas behandelt werden, das Kohlenoxyd enthält.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Nahrungsmittel mit einem Gas behandelt werden, das auch ein Reduktionsgas enthält, das aus der Gruppe Schwefelsäureanhydrid, Wasserstoff und Stickstoffoxyd ausgewählt wird.

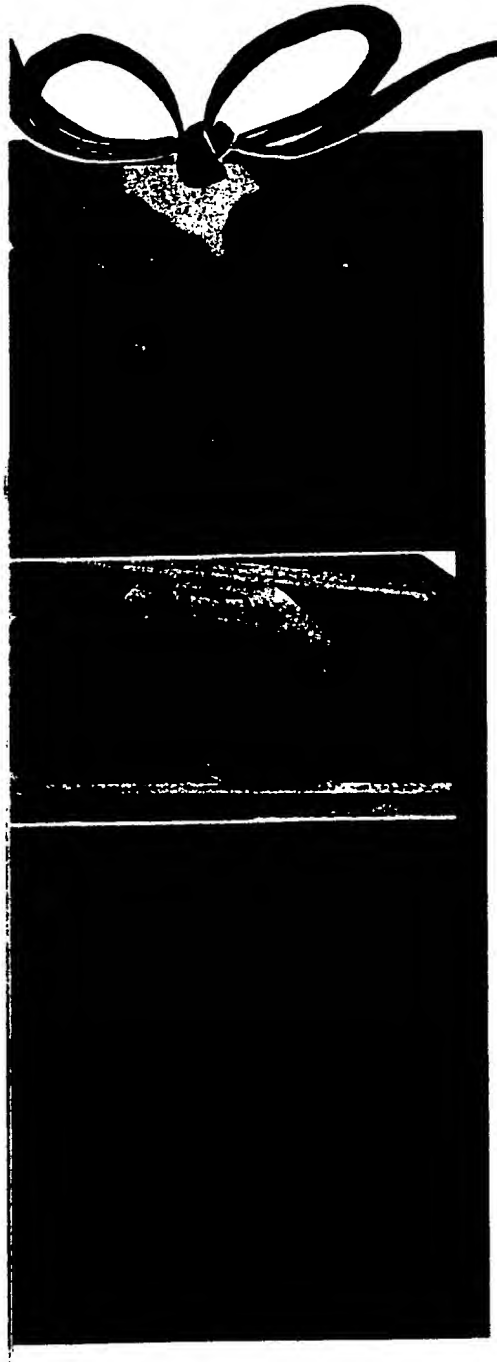
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß ein Gas benutzt wird, das auch ein neutrales Gas enthält.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß ein neutrales Gas verwendet wird, das aus der Gruppe Stickstoff und Kohlensäureanhydrid ausgewählt wird.

5. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß vor der Gasbehandlung die Nahrungsmittel einer Vakuumbehandlung unterzogen werden.

6. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß Leuchtgas verwendet wird.

7. Nahrungsmittel, gekennzeichnet durch die Behandlung mit dem in einem oder mehreren der vorhergehenden Ansprüche erläuterten Verfahren.



Controlled & modified atmosphere packaging

Methods for extending shelf life of a variety of food products

FRAN LABELL, Eastern Editor

The International Conference on Controlled Atmosphere Packaging convened in Chicago this past Autumn, under the sponsorship of Schotland Business Research, Inc. Several speakers discussed the current benefits and predicted future impact of controlled and modified atmosphere packaging on various food industry segments—including meats, seafoods, baked goods, and fresh fruits and vegetables.

Baked goods

Mold growth is a major factor in the shelf life of baked products, David Seiler, principal scientific officer, Flour Milling & Baking Research Association, Chorleywood, Herts., UK, told the group. Delaying mold growth permits a longer shelf life and aids production economy. It also permits the baker to make higher-moisture products and to use fewer preservatives. To inhibit mold growth, a package can be purged with an inert gas such as nitrogen and maintained at a 98% nitrogen level. Carbon dioxide can be used for its intrinsic mold-preventing characteristics. A mixture of two gasses also can be used.

It is crucial to find material which will retain carbon dioxide long enough to extend shelf life. Packaging material is less permeable to nitrogen than to carbon dioxide, so carbon dioxide is lost more quickly. Chilled products need less carbon dioxide than products at ambient temperatures. Form-fill-seal is a good packaging method for baked goods, because it makes packages of various sizes using many materials. However, it is important to get a tight seal, because there can be problems with leakage where layers of film are sealed. To detect leaking packages, a carbon dioxide sniffer, which detects leaks in a pressurized atmosphere, can be used. A short heat treatment causes properly sealed packages to swell up. A pH indicator relates to carbon dioxide concentration.

The correct gas or mixture of gasses and the right packaging equipment can prevent most molding of baked goods, said Andrew Benson, Sales Manager, Rose Forgrove, Inc., Elmhurst, IL. He cited examples of sliced bread with a shelf life up to 4 weeks; hamburger buns, hot dog rolls, and specialty breads with a shelf life up to 3 months; English muffins and cake, up to 6 months; and cookies, over 6 months.

The correct barrier will protect aroma, flavor, and moisture retention, but will have no effect on syneresis, Benson warned. The barrier proper-

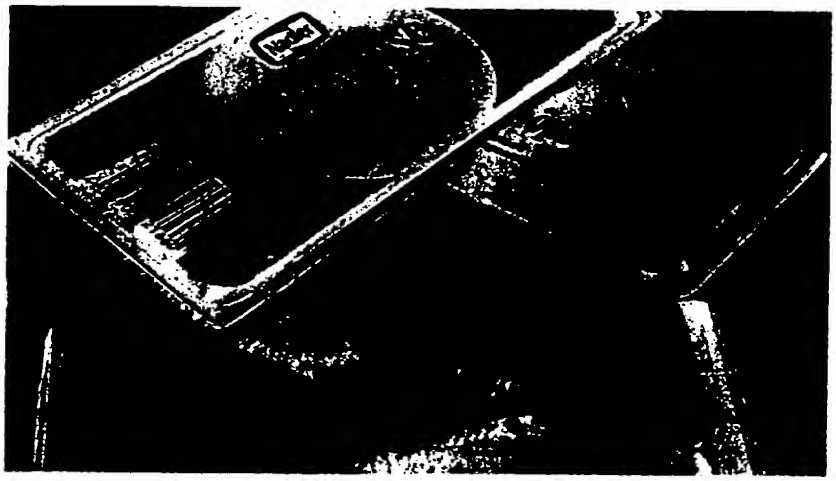
■ *As a point of reference, Dr. Daniel Farkas, Chairman of the Food Science & Human Nutrition Dept., University of Delaware, defines the two terms: Controlled atmosphere—The addition at the time of package closure of a reagent (for example, an oxygen-absorbent scavenger) to actively control the gaseous environment surrounding a food which is respiring or changing chemically. Modified atmosphere—The insertion at the time of package closure of an inert gaseous environment (for exampl , a nitrogen purge), so that shelf life will be extended by reducing the reactivity of the food contents.*

Three examples of thermoformed, controlled atmosphere packaging . . .

Fresh, unfrozen French fries packaged in Holland

Fresh tortellini pasta packed in a nitrogen/ carbon dioxide gas mix. Photos courtesy of Koch Supplies, Inc.

Pickled herring packaged by a German processor



ties of the wrapping material are crucial, as are the closure system and the ability of the packaging machine to purge oxygen from the package and replace it with the desired gasses. Seams on packages must be leak-proof, he stressed. Accurate time and temperature control must be used in forming the long seal.

Fresh produce

Controlled or modified atmosphere packaging treats a fresh fruit or vegetable as a living system, taking into account its respiration, Dr. Steven Wolfe, Fresh Western Marketing, Salinas, CA, told the conference attendees. Atmosphere modification can help maintain quality and prolong shelf life, inhibit pathogens, and reduce respiration rate, Dr. Wolfe said. He pointed out that most fresh produce now spends 3-14 days in the distribution channel, most of it without controlled temperature or atmosphere. This leaves a minimal shelf life, once the product gets to market.

Controlled atmosphere packaging is superior to modified atmosphere packaging in extending shelf life, Wolfe said, but suggested that the small extension may not be worth the cost in many cases.

Dr. Syed Rizvi, Associate Professor, Dept. of Food Science, Cornell University, told the group that apples stored under modified atmosphere conditions stay fresh up to 10 months in bulk—but, once they are out of storage, they have no protection. In cooperation with Cryovac, he has experimented with modified atmosphere packaging of apples, and found that it is possible to extend their shelf life from one week to 4-6 weeks.

Film permeability & package headspace

Dr. Rizvi finds that film of the proper permeability and minimum headspace help to accomplish this packaged apple shelf life extension. "One must increase carbon dioxide or decrease oxygen to slow down respiration according to the sensitivity of the commodity," Rizvi said. He recommends vacuum packaging or shrink wrapping the fruit to get a small headspace and to rapidly establish modified atmosphere.

Dr. Rizvi has worked out a mathematical model of the modified atmosphere system to help determine the necessary permeability of the film. It takes into account permeation of gas, surface area of fruit, headspace, rate of respiration, and temperature distribution. Rizvi suggests that, if the quality retention needs of the fruit are calculated, it is possible to design a film of the right permeability.

He compared apples which were freshly harvested, those held in cold storage for 4 months, and others vacuum packaged with 3-4cc headspace

and held for 4 months at 3 different temperatures and relative humidities. He found less weight loss and greater shelf life with the film-wrapped apples. In consumer tests in the Syracuse area, respondents said that the film-wrapped apples looked and tasted fresher and had a more attractive appearance than non-packaged ones. Negative comments were that the packages were difficult to open and that the apples had a slight "plastic taste."

Roger Rij, Agricultural Marketing Specialist, USDA, Fresno, CA, told the group that of the $7.7 billion worth of fresh produce grown in the United States each year, about 12% is lost during distribution—as a result of fungus, mechanical injury, and physiological problems such as decay. Holding produce at the optimum temperature is the most important factor in reducing loss, but this is difficult in our long, complex marketing system, he said. Modified atmosphere packaging could reduce loss because it changes the metabolism of the produce and inhibits ripening and pathological breakdown, according to Rij.

He reported on experiments he conducted with modified atmosphere packaging of broccoli. Two PVC films with different carbon dioxide transmission rates were used to overwrap broccoli in trays. Unwrapped broccoli and wrapped broccoli were held at 7.5 C and 5 C, the optimum temperature for broccoli, for 3 weeks. The carbon dioxide levels inside the film wrapped packages differed little at the two different temperatures. Researchers checked for color, compactness, decay, odor, and flavor before and after cooking, general appearance, and weight loss. The control had significantly more weight loss than the wrapped broccoli. It also showed more effects of ripening, and even decay. The results were significantly better with both films. Both films gave slightly better results at 5 degrees than at 7.5 degrees. The packaging must be designed for the commodity, Mr. Rij stressed. It is important to look at the mechanisms of the produce and the packaging material.

Low-density blown polyethylene film can be used in modified atmosphere packaging as an inexpensive, but effective material, according to Richard Pumala of Shields Bag & Printing Co., Yakima, WA. He gave several examples of how polyethylene material in combination with high carbon dioxide atmosphere can extend the shelf life of some fruits. Kiwi fruit, grown in California, is a soft fruit which cannot be stored in bulk, and it produces ethylene gas as it ripens. Using a polyethylene liner in kiwi shipping containers with a high carbon dioxide atmosphere helps prevent ethylene production and contributes to a 6-month shelf life.

Cherries harvested in the Pacific Northwest have a short, hectic marketing season. Sixty percent of the crop is shipped in two weeks. Ripening can be retarded and moisture loss reduced, if cherries are cooled soon after picking and placed in LDPE-lined cartons vented at the bottom to allow moisture to escape. Large, crisp fruit are the best candidates for this treatment. In this case, modified atmosphere packaging can help extend the marketing period, Mr. Pumala said.

Meats, seafoods, salads

Fresh foods such as salads, fresh and processed meats, poultry and fish, pasta, sandwiches, and snacks also can be given an extended shelf life with controlled atmosphere packaging. At an earlier Schotland-sponsored conference, Lawrence D. Starr, President of Koch Supplies, Inc., described how packages are produced on automatic web-fed thermoforming machinery, gas-flushed, and hermetically sealed. In most cases, the objective is to remove the oxygen from the package to prevent oxidizing of flavors and growth of yeasts, mold, and bacteria. The oxygen is replaced with nitrogen, which provides a counter pressure against the physical effects of a vacuum, or with carbon dioxide which is used for its properties as an inhibitor of the growth of microorganisms. With fresh meats, fish, and poultry, some oxygen is used in the gas mix to preserve fresh product appearance and to slow the growth of certain bacteria.

"Freshness and absence of extraneous processing are attributes long desired and now possible"

Lawrence Starr
President, Koch Supplies, Inc.

A very interesting example of the shelf-life-extending capabilities of controlled atmosphere packaging is demonstrated in fresh pasta. Said Mr. Starr, "Fresh pasta is . . . we believe, on the threshold of significant growth in the United States. If you have never prepared or eaten fresh pasta, you are in for a treat. This type of pasta cooks in only half a minute to a minute and a half, contrasting with a 10-15 minute cook, depending on thickness, for the more familiar dried pasta.

"Shelf life for unpackaged fresh pasta, refrigerated, is normally 2-3 days. Using nitrogen or mixes of nitrogen and carbon dioxide, shelf lives of 3-4 weeks are possible."

In concluding, Mr. Starr said that controlled gas atmosphere packaging "meets a need for foods with characteristics superior to frozen or canned. It offers fresh foods with extended shelf life, and greater convenience and appeal. Freshness and absence of extraneous processing are attributes long desired and now possible." END

Additional information about controlled atmosphere packaging equipment may be obtaned from Koch Supplies Inc., 1411 W. 29th St., Kansas City, MO 64108.

Circle 573 opposite last page.

. . . and from Rose Forgrove Inc., 539 W. Wrightwood Ave., Elmhurst, IL 60126.

Circle 574 opposite last page.

Copies of the entire CAP '84 Conference procedings are available for purchase. Price and ordering information may be obtained from Schotland Business Research, Inc., P.O. Box 511, Princeton, NJ 08542.

Circle 575 opposite last page.

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Metmyoglobin Formation in Beef Stored in Carbon Dioxide Enriched and Oxygen Depleted Atmospheres

SUMMARY—A spectroreflectometric technique was used to determine the relative percentages of three myoglobin pigments, reduced myoglobin, oxymyoglobin and metmyoglobin at the surface of fresh beef. It was shown that, at constant humidity, the formation of metmyoglobin in beef was maximal at 6 ± 3 mm Hg of oxygen at 0°C and 7.5 ± 3 mm Hg at 7°C for semitendinosus muscles. Carbon dioxide concentrations of 10% and higher had negligible effect on the formation of metmyoglobin, provided the oxygen pressure was above about 5%. At high partial pressures of carbon dioxide, absorption of carbon dioxide increased and the pH of the surface decreased. In air, the formation of metmyoglobin varied widely from muscle to muscle.

INTRODUCTION

FOR TENDERIZING fresh beef by aging, it is necessary to hold the meat at temperatures above the freezing point for several days. Maximal tenderization is obtained at 0 to 2°C in about 14 days, shorter times being adequate at higher temperatures (Kuprianoff, 1964). At these temperatures bacterial spoilage is dependent on the initial population density. Extending storage life by using low relative humidities (Scott, 1936) leads to marked weight loss and discoloration. Haines (1933) and Scott (1938) extended the life of fresh meat by storage in selected atmospheres, low in oxygen and/or enriched with carbon dioxide. The present work was undertaken to determine if any undesirable color changes occurred in beef muscle stored at low oxygen and/or high carbon dioxide partial pressures, at a high relative humidity.

Any undesirable color changes will attain increased significance as the size of the joint decreases, thus if half or quarter carcasses are aged any surface discoloration will be relatively unimportant after butchering for retail consumption. Limitations on storage space often make this method of aging uneconomical and there is an increasing tendency to age in boneless, retail size cuts. Under these conditions surface discolorations are of major importance.

In sterile meat, of normal water content, the color is due mainly to the heme proteins myoglobin and hemoglobin. At a high relative humidity (99.3%), any discoloration of sterile, post-rigor meat is due to the oxidation of these pigments to the brown metmyoglobin and methemoglobin. (Myoglobin is the major colored protein in fresh beef and the color changes of myoglobin and hemoglobin are, to a first approximation, the same. Consequently the pigment states are generally analyzed in terms of myoglobin derivatives.)

Little objective work has been performed on the effect of carbon dioxide on color of fresh meat. Brooks (1933) found that up to 20% carbon dioxide (in air) had negligible effect on the oxidation of heme pigments in meat although 30% led to a slightly increased rate of oxidation, which he attributed to the reduced oxygen partial pressure. Brooks (1931, 1935) working with ox-blood (hemoglobin), and George et al. (1952a, 1952b) using pure horse heart myoglobin, found the rate of oxidation to be very dependent on the partial pressure of oxygen in the system. The rate was maximal at low partial pressure.

In meat the situation is more complex because (a) the oxidation is quasi-reversible as the enzymatic reduction of metmyoglobin to one of the reduced forms can occur (Stewart et al., 1965b), and (b) it is extremely difficult to determine, accurately and non-destructively, the pigment states at the meat surface. In the analysis of the pigment states in meat, extraction procedures are cumbersome; they destroy the sample analyzed and possibly cause changes in the relative proportions of the three pigments. For these reasons a spectroreflectometric method of analysis was preferred.

The three myoglobin pigments, both in meat and in solution, have an isosbestic point at 525 nm (Stewart et al., 1965b). Stewart et al. (1965a) estimated the percentage metmyoglobin at the surface of minced meat samples from the ratio of K/S values at 572 nm (an isosbestic point for reduced myoglobin and oxymyoglobin) to that at 525 nm. K/S is defined as

$$\frac{(1 - R\infty)^2}{2R\infty}$$ (Kubelka et al., 1931)

where $R\infty$ is the reflectivity of an opaque sample of such a thickness that there is no further change in reflectivity when the thickness is increased further.

This technique corrects for any difference in the total concentration of myoglobin pigments in the sample, but does not adequately allow for differences in the scattering (S) and absorption (K) coefficients of the meat matrix itself. Either one or both these coefficients will vary with pH, fat content, surface geometry and water content of the sample, as well as with the incident wavelength. The effects are such that the ratios of K/S at 572 nm to K/S at 525 nm are unlikely to be constant for "pigment free meat."

Snyder (1965) attempted to overcome the problem by adjusting all his spectral curves to a common reflectance (in absorbance units) of $R_A = 1.0$ at 525 nm, and estimating the metmyoglobin content by the reflectance at 572 nm. Unfortunately his plot of R_A at 572 nm against percent metmyoglobin, for known mixtures of oxymyoglobin and metmyoglobin in an aqueous suspension of dried milk was not linear.

Using these data Snyder et al. (1967) found that when K/S at 572 nm was plotted against metmyoglobin concentration the predicted linear relationship was obtained. They also found, for 18 beef rounds of known pigment state, that determinations of surface metmyoglobin concentration from the ratio of K/S values at 572 and 525 nm and from the K/S value at 572 nm after adjustment of R_A at 525 nm to 1.0 were equally accurate although, conceptually, they considered the ratio method to be preferable.

EXPERIMENTAL

Preparation of sterile samples

Discs of 14 mm radius and 15 ± 1 mm thickness were cut under aseptic conditions from a semitendinosus muscle which had been removed from the carcass directly after slaughter. Muscle was extensively flamed and aged for 2 days at 0°C in a closed, sterile container. These discs were used in the storage experiments. In initial experiments heme pigments in some of these discs were converted to 100 or 0% metmyoglobin by the action of ferricyanide (1%) and dithionite (20%) respectively. Other discs were minced and adjusted to various pH values

in the range 5.3 to 6.8 with M HCl and M NaOH before the pigments were converted to 100 or 0% metmyoglobin.

Gaseous atmospheres

A continuous flow of air or nitrogen (both containing 10% carbon dioxide), maintained at a relative humidity of 99.3% by bubbling through towers containing 0.2*M* sodium chloride solution, was passed through the container holding the samples. The whole system was sterilized before use. Microbial contaminants in incoming gases were removed by passing the gases through cotton wool plugs. Each system was stored in a room kept at the appropriate temperature (0 or 7°C). Air controls were stored under similar conditions. At least 9 samples were stored in each container.

In some experiments meat slices of radius 38 mm were stored in closed, sterile, plastic containers leaving a headspace of 18 ± 1 cc. Headspace samples were removed through sub-a-seals. A flushing arrangement through the seal allowed the gas composition in the headspace to be adjusted at will.

Spectral analysis, gas analysis and pH

The reflectance spectra of the meat samples were recorded against a magnesium oxide standard on a Hitachi Perkin-Elmer Spectrophotometer, Model 139, with reflectance attachment. The range scanned was 380 to 770 nm. After storage all samples were exposed to air (R.H. 99.3%) for 2–3 hr, at the storage temperature, so that any reduced myoglobin at the surface was oxygenated while avoiding any detectable change in the surface concentration of metmyoglobin. Spectra of the exposed meat surfaces were then recorded at 8 ± 1° C. Samples were contained in stainless steel cups of appropriate dimensions.

Gas analyses were performed at regular intervals using a 25V Fisher Gas Partitioner calibrated with purified gases. One tenth ml samples of gas, extracted with SGE gas tight syringes, were used. Average equilibrium concentrations are reported.

Surface pH was measured with a surface electrode and Radiometer Model TTT IC Titrator and pH meter.

Heme pigment concentration was measured according to the method of Hornsey (1956).

RESULTS & DISCUSSION

Determination of metmyoglobin at the surface

In preliminary experiments, minced semitendinosus samples, of known pigment state and different pH values were analyzed. In these the ratio of K/S at 572 nm to K/S at 525 nm, for 100% and 0% metmyoglobin varied and there was slightly better consistency in the K/S values at 572 nm when R_A at 525 nm was adjusted to 1.0 absorbancy units. Results obtained with several intact semitendinosus samples of known pigment state were consistent with those obtained on minced samples.

For 18 samples the K/S values at 572 nm, after adjustment of R_A to 1.0 at 525 nm, were respectively 2.41 ± 0.19 (range 2.15–2.62) and 6.05 ± 0.18 (range 5.80–6.30) for 100% and 0% metmyoglobin. Assuming the linear relationship between the adjusted K/S value at 572 nm and the percentage metmyoglobin, it was possible to calculate metmyoglobin as a percentage of the total surface pigments to within ±5%. The ratio of K/S at 572 nm to K/S at 525 nm yielded values of 1.450 ± 0.061 and 0.615 ± 0.050 respectively for 100% and 0% metmyoglobin, enabling the metmyoglobin at the surface to be calculated to within 6 or 7%.

As errors, determined by standard deviations, were greater using the ratio method the adjustment technique w used in the present study. The values o tained were independent of the area illumination, whether the surface p sented to the integrating sphere was fl convex or concave.

Differences in spectra due to variatio in total pigment concentrations are n climinated by this technique, but calcul tions showed that differences by a fact of 2 in total concentration should lead errors within the range of those found e perimentally. Pigment concentratio were always within the range 4.6–6.9 n per g of wet tissue for the different mu cles studied.

Another error can arise from the fa that intramuscular fat has a characteris spectrum. Thus it is unlikely that musc with different fat contents can be cor pared by this technique, as the "pigmen free" meats will not yield the appro mately parallel reflectance curves (i absorbancy units) that are necessary f this method to be valid. All the spectr determined, on meat of known pigme state, were found to be superimposabl to at least ±4% of R_A in the range 47(650 nm, and so it would appear that var ations in the fat contents of the lean mu cles studied were not of major importanc

In meat, oxymyoglobin and metmyo globin have an isosbestic point at 474 n (Stewart et al., 1965b) and all the abo arguments were found to be valid, e abling the percent reduced myoglobin the surface to be determined. The a justed K/S values at 474 nm were 2.0 ± 0.09 (range 1.90–2.12) and 3.88 0.10 (range 3.70–4.05) for 100% an 0% of the reduced pigment respectivel This enables percent of reduced myo

globin to be about 5%.

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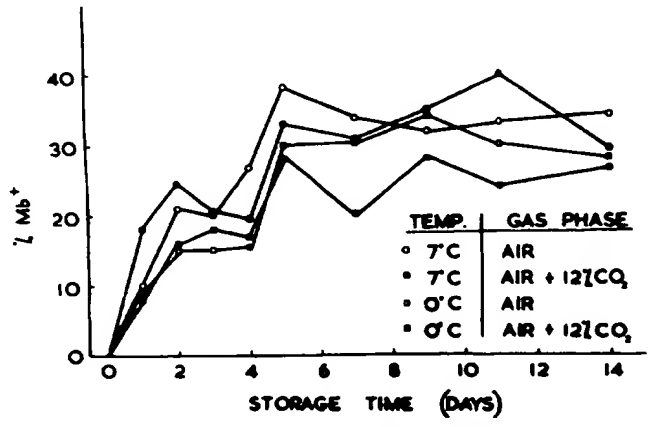

Fig. 1—The effect of 12.0 ± 0.5% CO_2 on the formation of metmyoglobin (Mb⁺) at 0°C and 7°C, on a sterile muscle (pH 5.58) at a relative humidity of 99.3%.

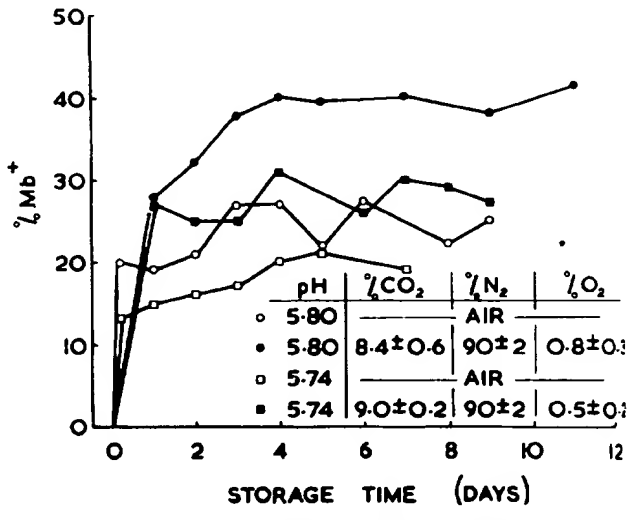

Fig. 2—The formation of Mb⁺ at 7°C, on sterile muscles i various atmospheres at a relative humidity of 99.3%. Sampli was discontinued when unavoidable contamination occurred.

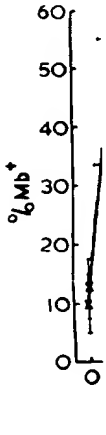

Fig. 3— gen and I storage fo

globin to be determined to an accuracy of about 5%.

Effect of storage on formation of metmyoglobin

Figure 1 shows the change in surface metmyoglobin concentration as a function of time for samples from the same muscle (pH 5.58) stored in air or 12% CO_2/air at 0 or 7°C and a R.H. of 99.3%. Figure 2 is a similar plot for samples of two muscles (pH 5.80 and 5.74) stored in the atmospheres indicated, at 7°C. At 0°C metmyoglobin formation in these samples was also greater at the lower oxygen partial pressures.

From Figure 1 it is seen that the presence of 12% carbon dioxide had negligible effect upon the formation of metmyoglobin. This was in accord with the observation of Brooks (1933). The increased oxidation found at the lower oxygen partial pressures (Fig. 2) was in general agreement with data obtained by Brooks (1935) and George et al. (1952b) with aqueous hemoglobin and myoglobin solutions.

Figures 1 and 2 both indicate that concentration of metmyoglobin was virtually constant after storage for 5 days.

When the freshly cut meat slices were sealed in the containers, concentration of carbon dioxide rose to between 10% and 15% while concentration of oxygen fell. Equilibrium was established within 48 hr. To ensure equilibrium, samples were stored for 12 ± 2 days, actual storage time governed by practical expediency. In a few instances pressure in the container was reduced by removing a measured volume of gas. In one experiment, muscle was sliced and packed in a nitrogen atmosphere so that the final atmosphere consisted solely of nitrogen and carbon dioxide.

The relationships between metmyoglobin concentration and partial pressure of oxygen, at 7 and 0°C, are summarized in Figures 3 and 4. All values are the means obtained for duplicate samples from the same slice.

Table 1—"Equilibrium" concentration of metmyoglobin for different muscles after storage in air for 12 ± 2 days.

Surface pH of the muscle	"Equilibrium" percent Mb^{+}[1] at the surface	
	7°C	0°C
1. 5.58	35 ± 4	31 ± 5
2. 5.60	22 ± 4	18 ± 4
3. 5.60	[2]	33.5 ± 5
4. 5.70	38 ± 5	31.5 ± 5
5. 5.74	20 ± 4	22 ± 4
6. 5.80	26 ± 4	31.5 ± 5
5.70	—	38.5 ± 4[3]
5.72	—	28 ± 3[3]
Av.	28.2 ± 8	Av. 26.3 ± 6

[1] Mb^{+} = metmyoglobin.
[2] Not measured—sample contaminated.
[3] Values not included in the average as these muscles were not used in the experiments reported in Figures 3 and 4.

The lower equilibrium concentrations of surface metmyoglobin on samples stored in air, were independent of pH (Table 1).

Brooks (1931) found that rate of oxidation of different samples of ox-blood, at 25°C and constant pH and ionic strength, varied greatly. The present results on meat (Table 1) show similar differences in that the equilibrium concentrations of metmyoglobin vary for different samples, the variation not appearing to be a function of pH. These differences may be explained by differences in rate of enzymatic reduction of metmyoglobin. Stewart et al. (1965b) have shown that the metmyoglobin reducing activity of different samples of ground beef can vary considerably under identical storage conditions.

The data reported by Stewart et al. (1965b) were obtained on metmyoglobin formed by ferricyanide oxidation and may not represent the true reduction of naturally formed metmyoglobin as ferrocyanide forms a complex with ferric heme pigments, this complex catalyzing the enzymatic reduction (Hegesh et al., 1967).

Recently several studies on the enzymatic reduction of ferric heme pigments have been reported and present evidence indicates that NADH plays a vital role (Hegesh et al., 1967), (Watts et al., 1966). Therefore the differences may represent different "NADH ferrihemoglobin and ferrimyoglobin reductase" activities in the muscle. No corrections have been applied to the experimentally determined metmyoglobin concentrations in Figures 3 and 4 to allow for the variations found in the air controls. If, however, corrections were made the fundamental character of plots was unchanged.

Figures 3 and 4 indicate that formation of metmyoglobin was maximal at a partial pressure of oxygen of 7.5 ± 3 mm Hg at 7°C and 6 ± 3 mm Hg at 0°C for the semitendinosus muscles studied. George et al. (1952b) found, for pure myoglobin solutions, that rate of autoxidation was maximal at about 1 mm Hg of oxygen at 30°C and pH 5.69. Brooks (1931) found rate to be maximal at 20 mm Hg of oxygen for ox-

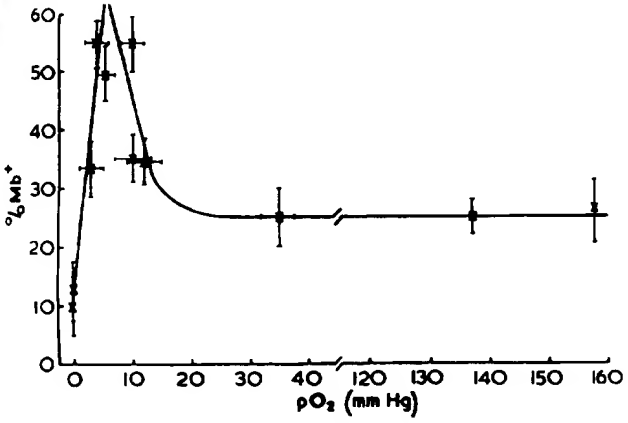

Fig. 3—The relationship between the partial pressure of oxygen and Mb^{+} formation at the surface of sterile muscles after storage for 12 ± 2 days at 0°C.

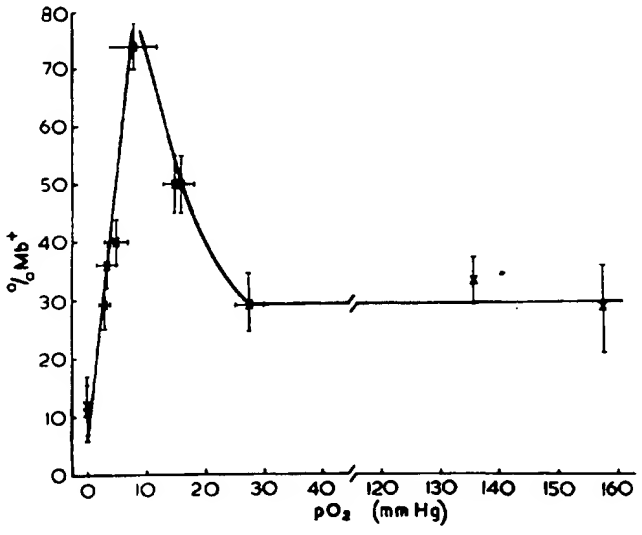

Fig. 4—The relationship between the partial pressure of oxygen and Mb^{+} formation at the surface of sterile muscles after storage for 12 ± 2 days at 7°C.

Table 2—Effect of CO_2/air concentrations on the formation of metmyoglobin, during 14 days storage, at 0°C.

Pack no.	pCO_2 init. mm Hg	pO_2 init. mm Hg	pCO_2 final mm Hg	pO_2 final mm Hg	ΔpH[1]	Conc. Mb^+ %
1	79	106	63	86	0.03	26.0
2[2]	167	82	46	109	0	29.5
3	190	84	127	84	0.05	32.0
4	273	68	167	74	0.06	32.0
5	312	61	209	68	0.06	31.5
6	403	53	244	64	0.07	31.0
7	471	38	283	59	0.08	36.0
8	578	30	307	50	0.09	40.0
9	669	15	384	41	0.07	63.5 (2.5 hr) 52.0 (24 hr)
10	730	0	535	22	0.12	70.0 (2.5 hr) 51.0 (24 hr)

[1] ΔpH was the increase in surface pH of the samples upon removal from storage; the pH returned to its original value within 2 hr.
[2] Pack 2 leaked slowly with time.

Table 3—Effect of CO_2 pressure on th formation of metmyoglobin at 0°C.

pCO_2 mm Hg	pO_2 mm Hg	ΔpH[1]	"Eq. Conc." of Mb^+
0	152	—	38.5
76	135	0.06	42.0
190	104	0.05	39.0
380	76	0.06	43.0
510	56	0.10	43.0
650	110	0.27	39.5

[1] ΔpH is as per Table 2.

blood (hemoglobin) at 25°C and pH 5.69.

If the ratio of myoglobin to hemoglobin varied to a marked degree between the muscles studied, a comparison of results would not be valid when expressed as a function of the oxygen partial pressure. It was considered unlikely that such variations occurred. At low oxygen partial pressures, rates of both the autoxidation and enzymatic reductions are increased (Watts et al., 1966). The present results show that increase in rate of oxidation, at 0 and 7°C, is greater than any increase in the enzymatic reduction at the low oxygen pressures studied (Figs. 3 and 4).

This maximal formation of metmyoglobin occurs in all samples, independent of external oxygen pressure, provided this is above the critical value. However, with higher oxygen partial pressures the formation will occur below the surface, the depth at 0°C being about 5 mm in air and varying as the square root of the external oxygen pressure (Brooks, 1929). At the lower oxygen partial pressures the metmyoglobin layer will thus be nearer the surface until, at the critical partial pressure, it is at the surface.

When transferred from the oxygen depleted atmospheres to air, samples with high metmyoglobin contents tended to be reduced with time. This reduction was always very slow, the maximum reduction observed within 24 hr being from 72 to 63% at 7°C with no measurable reduction within this period at 0°C (less than 5% at 55% concentration).

Effect of increased carbon dioxide concentrations

Sterile samples were packed in sealed containers, in atmospheres of various carbon dioxide partial pressures at 0°C. Before packing the samples were left in air for 3–4 hr at 0°C to allow most of the physically bound carbon dioxide to be released. The volume of meat was 25 cc and the total volume 85 cc. In all cases the carbon dioxide concentrations fell due to absorption while the oxygen and nitrogen levels rose. Equilibrium was reached at 24–48 hr. The results are summarized in Table 2.

The values given for the percent of metmyoglobin quoted for the two higher concentrations of carbon dioxide are the values obtained after exposure to air for 2 hr, as reduction occurred over 24 hr (Table 2). All other values are averages of 4 readings, 2 on each of 2 samples, at 2.5 and 24 hr. These results indicate that at the higher carbon dioxide and lower oxygen partial pressures the formation of metmyoglobin increased, presumably due to the decreased oxygen pressures.

The reduction of metmyoglobin found in packs 9 and 10 on exposure to air was greater than any reduction that occurred after storage in 10% carbon dioxide/nitrogen mixtures. Although variations between muscles are to be expected the decrease in pH during storage in high carbon dioxide concentrations (Table 2) may also help to explain this, as autoxidation is accelerated at lower pH values (Brooks, 1931) while enzymatic reduction is retarded (Stewart et al., 1965b).

The initial nonequilibrium of the gas phase in these packs made interpretation of results difficult due to the interrelation between decreased pH and oxygen pressure. In further experiments at 0°C various equilibrium gas phases of carbon dioxide/oxygen were used. The oxygen pressure was always above the level necessary to cause increased metmyoglobin formation. Increasing the carbon dioxide pressure, at 0°C, had no effect on formation of metmyoglobin during 15 day storage even though the pH of the meat was markedly decreased (Table 3).

No measurable change occurred in the surface concentrations of metmyoglobin on re-exposure to air, at the relatively low concentrations of metmyoglobin used in this experiment.

In the first experiment, the meat in higher carbon dioxide atmospheres developed a greyish tinge, which masked the natural "redness" of the meat. This may have been due to decreased pH of the meat causing some of the sarcoplasmic proteins to undergo post-rigor isoelectric precipitation. In the second experiment, even though the muscle was of similar pH (5.72 and 5.70), the meat appeared "normal" at all the carbon dioxide pressures studied. In subsequent experiments this "greying" phenomenon has been observed in samples stored for 14 and 28 days in 60% carbon dioxide atmospheres, but no explanation can be offered for its occurrence in only certain muscles.

From the results described in the present paper it would appear that the storage of sterile beef in carbon dioxide enriched atmospheres leads to no increased metmyoglobin formation, provided the oxygen partial pressure is maintained above a limiting value of about 5%.

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Comparison of Carbonyl Compounds in Moldy and Non-moldy Cocoa Beans

SUMMARY—Carbonyl compounds in moldy and non-moldy cocoa beans were converted to dinitrophenylhydrazones and separated into monocarbonyl classes. Growth of mold was always accompanied by relatively large increases in carbonyl concentrations. Increases in total monocarbonyl values ranged from 20 to 500% and averaged almost 300% for the eight pairs of samples analyzed. Compared to non-moldy beans, moldy cocoa beans contained greater concentrations of methyl ketones, 2-enals and 2,4-dienals, but saturated aldehyde concentrations were quite often lower. TLC revealed the presence of C_5, C_{11}, C_9, C_{17} and several unidentified methyl ketones. Most of the ketones detected in moldy beans were also found in non-moldy beans but in lower concentrations. Qualitatively, the unsaturated aldehyde fractions varied considerably among samples. 2-Pentenal and 2,4-pentadienal appeared as prominent TLC spots and other 2-enals and 2,4-dienals were frequently observed in moldy beans. The only unsaturated aldehydes detected in non-moldy beans by TLC were 2-pentenal and 2,4-octadienal.

INTRODUCTION

CONDITIONS for mold attack in the tropics are favorable in damaged or improperly dried cocoa beans. It would be expected that beans are normally highly infested with mold spores and with an increase in moisture these spores may germinate and cause undesirable changes to occur.

Boyd, et al. (1965) in a study of the monocarbonyls of chocolate suggested that mold activity might have contributed significantly to the observed variation in methyl ketone content of cocoa beans. Unfortunately, these investigators did not have an opportunity to collect supporting data by analyzing moldy cocoa beans. It was envisioned that if Boyd's suggestion could be verified, a way might be opened for the development of an objective chemical procedure to replace the current subjective "cut test" for determining mold infestation. At present the cut test involves cutting the cocoa bean longitudinally and visually observing for mold.

The research reported in this paper concerns the differences in total carbonyls, total monocarbonyls and relatively concentrations of the different monocarbonyl classes in moldy and non-moldy cocoa beans. The data collected were based on the methods of Schwartz, et al. (1963) as modified for chocolate products by Boyd, et al. (1965). The techniques involved the conversion of carbonyls to 2,4-dinitrophenylhydrazones (DNP-hydrazones) followed by separation into the following classes: methyl ketones, saturated aldehydes, 2-enals and 2,4-dienals. Thin layer chromatography procedures of Schwartz, et al. (1968) were used to identify and assess the complexity of each class of monocarbonyls.

EXPERIMENTAL

Samples

Several samples of moldy cocoa beans, supplied by chocolate manufacturers, yielded unusually high carbonyl values. Since many variables affect carbonyl concentrations (Boyd, 1965), it was decided that the best experimental approach was to develop mold on beans under controlled laboratory conditions. This made possible comparison of carbonyl values before and after growth of mold, thereby minimizing the effect of many interfering variables.

Aspergillus and *Penicillium* were the two main types of mold isolated from cocoa beans and were used to inoculate non-moldy beans for control-molded samples. The *Aspergillus* and *Penicillium* spores were removed from moldy cocoa beans with sterile water and then inoculated onto cocoa beans using a sterile, platinum loop. The inoculated cocoa beans were placed in a 1 qt polyethylene container with a small mat of filter paper (1 in. × 1 in. × 1/4 in.) saturated with sterile water to induce mold growth. The beans were stored at approximately 24°C to facilitate mold growth and simulate tropical conditions. Cocoa beans from several of the major producing countries were included in the study.

Moldy beans were also obtained directly from the tropics through the cooperation of the Turrialba Experiment Station, Costa Rica. A batch of fermented Matima beans had been split and one portion dried under normal conditions while the other half was purposely kept from drying for several days to allow mold to grow. These samples made it possible to determine the changes which take place as a result of mold growth during the fermenting and drying stages.

Solvents

All solvents were freshly distilled and rendered carbonyl free (Schwartz, et al.,

Longer product shelf life using modified atmosphere packaging

By Nancy J. Muller

Nancy J. Muller, product manager, red meat packaging, Cryovac Division, W.R. Grace & Co., Duncan, S.C., presented this discussion of "Modified Atmosphere Packaging—Shelf Life Extension of Fresh Red Meats" at the recent Westpack Exposition in Anaheim, Calif.

I HAVE BEEN asked to speak on controlled atmosphere packaging for extending the shelf life of meats. I'm actually going to narrow my remarks to cover where gas flushing fits in among the available alternatives—both today and in the future.

The focus is primarily on retail packaging and the direct implications for wholesale or institutional applications and is on fresh red meats, unless specifically noted otherwise.

First, I want to share with you the marketplace considerations and driving forces behind the attention that this subject is receiving. How American consumers relate to shelf life extension options is of key interest to us at Cryovac. The shopper is the one variable ultimately reponsible for the success or failure of a program. So my notes cover research largely of a marketing type.

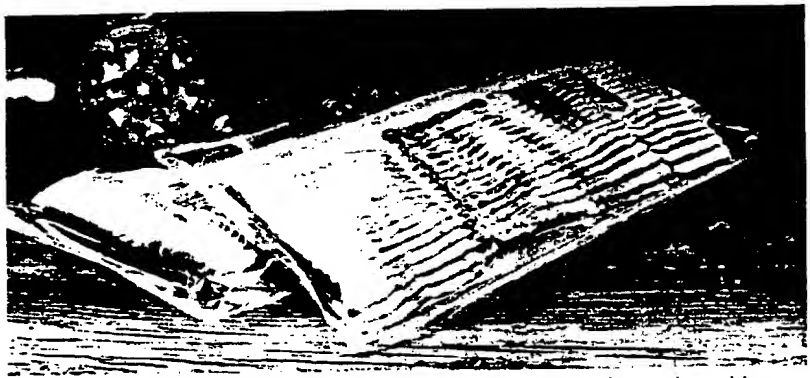
Let me first define some important terms. The terms "modified atmosphere" and "controlled atmosphere" should *not* be used interchangeably, even though they often are. Although packaging systems used in the future may, in fact, include controlled elements, what we generally have available to us today is modified atmosphere packaging. The difference between the two lies in the dynamic nature of the food package's interaction with both its contents and its outside environment.

A control "system" must be added to the package for controlled atmosphere packaging. The "system" then can "sample" the gas, or atmosphere, around the food and determine the optimum condition needed to ensure maximum food quality. Gases are then added or removed to maintain a desired balance.

Fresh apples "suspended" in cold storage are an example of controlled conditions allowing changes in the respiring fruit to take place more slowly to preserve the fruit's freshness over a longer period. In this case, the bulk bin is part of the "packaging" or storage vessel. Here, we have a "closed system," so to speak, because the container is virtually impermeable. Valves are activated for sampling and adjusting the atmospheric conditions.

Modified atmosphere packaging represents most of what we as consumers encounter on "living" foods—that is to say, beef or cheese which is aging naturally, or breads and sweets which will grow stale over time. Here, the packaging film has some degree of permeability. Modified atmosphere packaging implies enclosing a product with some type of barrier and using a selected mix of gases such as nitrogen, oxygen, carbon dioxide and water vapor. During storage, these gases are free to react with the product and any microbes on its surface to retard product deterioration. Shelf life is thereby extended.

But the atmosphere of the package is only modified from the atmospheric air we breathe, and it is constantly changing because spoilage bacteria on the red meat and mold on the bakery products are not completely dormant. The point is, we are not *controlling* anything. What we've modi-



Modified atmosphere packaging can make slice peel-off easier for packaged bacon.

fied remains in a state of flux. Therefore, even vacuum packaging fits within the broad definition of modified atmosphere because the air around the product has been consciously altered.

I don't want to give the impression that modified atmosphere packaging is the only element in extending shelf life of fresh meats. It does not negate the need for sound sanitation practices and proper refrigeration. It will inhibit microbial growth but it won't kill microbes. It has been shown that even in the presence of CO_2, bacterial growth will increase rapidly at increased temperatures.

Meat to be packaged under modified atmosphere conditions should have a low bacterial count at the time of packaging and be well chilled, and refrigeration needs to be maintained during shipping and storage. The most sophisticated packaging made—today or in the future—will not erase the sins of negligent handling procedures.

Modified atmosphere packaging is not new despite the recently expanded interest in it. Basic research on fruits and vegetables dates back to the 1920s. In 1933, the first shipment of chilled beef under 10% CO_2 atmosphere was transported from New Zealand to the United Kingdom. By 1938, 26% of the beef from Australia and 60% of that from New Zealand was being shipped in refrigerated, gas-tight holds under a CO_2-enriched atmosphere. No bacterial spoilage was evident after 40 to 50 days on quarters or sides transported in this manner.

In Europe, Scandinavia and the U.K., its use is far more widespread today than in the U.S.

In Scandinavia and Europe, breads, cookies, cakes and other sweet goods represent an increasing commercial application. It has been estimated that up to 25% of all sweet goods in the U.K. are now packed in elevated CO_2 packages. Up to four days of mold-free shelf life is being achieved.

Bacon and luncheon meats are examples of processed meat items being gas flushed for easier slice separation.

Salads are being gas flushed for freshness in France and the U.K.

In France, poultry is being distributed in modified atmosphere packaging for foodservice and institutional uses.

ABOVE: With larger cuts of meat, modified atmosphere packaging can protect film from abrasion and punctures. BELOW: Protection to carton lot of fresh meats, such as pork loins, can be provided with current modified atmosphere technology.

Of course, Marks & Spencer, one of the largest retail chains in the U.K., has had a gas flushed ATMOS PAK type of package in its stores for all fresh meats since 1979. IRMA in Denmark offers a very similar package. Both clear and white bottom trays are being used.

Marks & Spencer has its packaging done by a carefully selected group of firms and quality control standards are rigidly enforced. IRMA, meanwhile, is a regional retailer with its own central prepackaging operations. IRMA stores are located within a 60-mile radius of the central facility, and delivery is typically available twice daily.

Here, in the U.S., tons of strawberries are being shipped from California using the TecTrol process—the gas flushing of packaged pallets. Fresh pasta, as well, is traveling in modified atmosphere. The marketplace is even witnessing chocolate chip cookies arriving in moisture-barrier flexible plastic pouches.

What is prompting all of the excitement in this country—and even abroad?

Certainly, as concentration in the supermarket and restaurant industries continues, the need for extending shelf life becomes more important. In the last five years, more than 5,500 conventional stores have closed. The top 10 chains now control $73,100,000,000 of retail food sales. The supermarket has a new face, too—one of "boutiques" for cheese,

Modified atmosphere packaging of retail fresh meats can extend the color retention and shelf life of the products.

meats, baked breads and even flowers. Accordingly, the industry is shifting its emphasis from in-house production to merchandising. And understandably, at least 80% of fresh meats are moving through some type of intermediate warehousing. Store-door delivery has become a luxury of the past.

The restaurant industry illustrates a similar story. The nation's restaurant food and drink sales represented by the top 10 chains today command over $100,000,000,000. The concentration is being seen not only in the purchasing and storage practices of the company-owned outlets but in that of the foodservice distributors themselves. In a recently completed Cryovac study on HRI meat buying practices, we learned that the average meat inventory turnover for foodservice is over three weeks. Add this to a minimum eight to 10 days for storage and transit from the packer, and we're looking at quite a demand for extended shelf life packaging.

Meanwhile, a crowded industry of meat packers is looking for value-added niches, with the hope of insuring their survival with improved margins. As a result, we've witnessed an interest in prepackaged consumer portions of meat. This, in turn, has prompted inquiries into alternative packaging materials and their potential effect on consumer demand. I'll touch on this point later, but suffice it to say that oxygen-rich atmospheres have a role to play.

Elsewhere, the tide against using chemical additives and mold inhibitors is growing. The "natural foods" cult has spread its influence from the generation of flower children to that of yuppies, as medical research continues to scrutinize the possible harmful effects of chemical preservatives and additives.

What does this trend have to do with packaging? It means that the demand for more sophisticated packaging will only increase as we seek to deliver to the consumer perishable foods which are fresh, tasty and appealing as well as convenient to their lifestyles.

What, then, are the major advantages of the modified atmosphere packaging technique which utilizes gas flushing?

1. For fresh red meats, sufficient levels of oxygen in a retail package can allow the meat to "bloom" into a bright red color that is associated by the American consumer with freshness.

2. Depending on the product, shelf life can be extended. In the case of fresh red meats, various experiments and studies have exhibited shelf life extensions of six to 10 days over conventional in-store film wrap which, based on experience, provides only three to four days.

3. Back flushing of gas allows us to manipulate the degree of cling of the packaging material to the product. For products which easily crush or that have shapes that are an integral part of the shopper's judgement on quality, this could well be an important attribute. For meats, of course, the consumer still has the need to recognize familiar shapes.

4. Because of the somewhat pillowy effect afforded by nitrogen, in particular, gas-flushed packages can be used successfully for sharp or abrasive products that would otherwise puncture collapsed films. Packers have long used this principle in shipping bone-in pork bulk-packed in nylon pouches. There is opportunity to do even more with this application

in the future.

Among its disadvantages are still cost considerations, not only of materials and gases but line speeds and labor requirements as well. Modified atmosphere packaging is bound to involve higher costs than conventional packaging on rollstock thermoform or horizontal form-fill-seal machines.

In addition, antifog agents are likely to be needed in films used on refrigerated products. This, depending on the material itself, could increase costs further.

Versatility of the package is questionable, in terms of accommodating different shapes and sizes of retail product. In an age when the strata of consumers are demanding more variety, care must be taken not to hamper the retailer's ability to respond. Obviously, this is a concern in prepackaging product that would otherwise be wrapped at the store level.

The shelf life of specialty products such as stuffed, boneless pork chops, can be extended through use of modified atmosphere packaging.

Space also is a common complaint in two regards. Because there is headspace required for the gas, packages have the appearance of being bulky and underfilled. The 2:1 package-to-product ratio can cause headaches for the retailer because he needs additional space for the same volume of product in his retail meat case or he must restock it more frequently. The package cannot be turned upside down without risking surface discoloration. Once in the consumer's home, space is of further concern for storage in the refrigerator. It is thus not well suited to shipping and freezing. Moreover, consumers in focus group interviews which Cryovac has conducted have questioned the ease of opening.

Most important, many have disapproved of its excessively expensive look. One lady in her late fifties and wearing a mink pillbox hat commented during a series of such interviews in Chicago that the retail, gas-flushed package for fresh meats looked like the "Neiman Marcus" of packaging and that she would prefer the "Marshall Field" version. That analogy puts it in a nutshell. There is, nevertheless, a segment of consumers turned on by its richness and gloss, suggesting something at least about the premium product inside that they would expect to see.

Let me digress here to speak about shelf life itself. We define the term at Cryovac not only in the laboratory but also in marketplace jargon. It reflects the amount of time that a product can be comfortably sold to the end user while it is still at a high level of freshness, good taste and eye appeal. It also includes enough lead time for the purchaser to take the product home and decide when to consume it.

Many consumers purchase for same-day consumption, while others are far more fickle about their evenings' plans. The package today, and especially in the future, has to be even more flexible and forgiving. There is no single stereotype of American consumer. The retail consumer audience is more fragmented than ever before. The package for fresh red meat for sale in the supermarket meat case must, therefore, be convenient—transparent, if you will—and in no way a hindrance to the shopper's decisions.

What, then, are shoppers looking for in fresh meat packaging?

Just that—convenience and transparency. The need to be free to throw it into the freezer without further rewrapping or handling. The package must have integrity and be leakproof. If an easy-open feature is noted, it has to be, in fact, easy to open. It must not complicate an already complex, harried life.

Future packaging needs to be microwavable and ovenable. It must have the retailer's endorsement and support, especially if it looks different in any way from the conventional package. In fact, we found, through probing questions during recent consumer research, that the retailer itself had more to do with the consumers' comfort level with different packaging alternatives than any other single variable.

Shoppers are increasingly accepting national brands. They don't resist the idea of central prepackaging of fresh meats a thousand miles away. They are, however, adamant about holding the retailer fully responsible for the quality of the product they receive. Thus, the retailer must be entirely comfortable with the product he is receiving and, in turn, offering for sale.

What does the future hold?

We are definitely due for enhancements in packages which can be hermetically sealed. Higher efficiencies in sealing equipment are also forthcoming as a greater variety of food applications are sought. Lower cost materials should also become available. Various levels of film permeability need to be tested. Various gas mixtures and different gases need to be investigated, especially in addressing the excessive headspace issue.

Even different oxygen removal vehicles will be used, which are not necessarily dependent upon the mechanics of equipment itself. Scavengers, for example, will become part of the packaging process. "Smart" films, of course, could also become part of our future. Talked about largely in academic circles, these films could respond to changes in gas concentrations in the package. They would then decrease or increase the gas by diffusion or chemical absorption.

What about all the other means of modifying atmosphere? Vacuum packaging could well overcome the problem of the purplish-red color which it maintains in meat by commercializing strippable or peelable barrier layers. This will allow the

An employee is shown positioning a pouched boneless chuck for modified atmosphere packaging. While most attention is paid to the shelf life extension, this type of packaging, of course, also eliminates chances of soiling.

product to "bloom" at an appropriate time and with the least sacrifice of shelf life. Of course, vacuum levels can be modified, too, depending on the product.

"Soft" vacuumizing heat seal equipment is currently available for certain cheese and vacuum skin packaging is even more appropriate for preserving the delicate shapes of product where distortion would be a serious deterrent to the retail shopper. The consumer does not want to learn a new alphabet of product shapes. The shopper wants simplified, not complicated, buying decisions. The less re-education necessary, the better.

The convenience and flexibility concerns can, perhaps, be most fully addressed by the newer cook-and-ship and cook-and-strip bag materials. Cryovac, along with several others, has developed a family of materials which can be cooked in water or in microwave or high-humidity ovens. Used in foodservice segments or translated into an appropriate consumer package, these materials offer virtually limitless market development opportunities.

What, then, is the answer? What is the future consumer package for fresh red meats? The answer probably is: all of the above and then some. Just as we expect to see a continued plethora of consumer products from which to choose, we can expect packaging to offer an equal degree of variety and experimentation. □

Flashes on Suppliers

Wixon Industries, Inc.: Chuck Ehemann has been appointed vice president of sales for this Milwaukee-based spices, seasonings and flavors firm. Also, William B. Bond, jr., was named vice president of manufacturing for the company's operations.

American Can Co.: Three executives have been promoted to the new position of senior vice president as part of a reorganization of this Greenwich, Conn., firm's packaging sector into three major business groups. According to John G. Polk, executive vice president and sector executive for packaging, the reorganization is intended to "further enhance our customer and market focus as well as concentrate our resources on the strategic and tactical objectives of our packaging businesses." Henry R. Martin, formerly vice president and general manager of flexible packaging, was named senior vice president, performance plastics packaging. John F. Hildner, formerly vice president and general manager of beverage packaging, was named senior vice president, beverage and international metal packaging. Douglas W. Moul, was named senior vice president, food/specialty and meat packaging, having formerly been vice president and general manager of these activities.

Frick Co.: Peter C. Spellar has been named president and chief operating officer of this manufacturer of industrial and commercial refrigeration products which is headquartered in Waynesboro, Pa. The announcement was made by Robert N. Pokelwaldt, chairman of the board. Spellar joined Frick in 1979 as vice president-engineering and had served as executive vice president since 1983.


SPELLAR

Curtice-Burns, Inc.: This firm, headquartered in Rochester, N.Y., has agreed to acquire the can making business of Borden, Inc., located in Lyons, N.Y., for an undisclosed price. The business will be conducted through Finger Lakes Packaging, a Curtice-Burns subsidiary. Mark Quinn, controller of the facility, will become general manager and chief executive officer, reporting to Roy Myers, vice president-operations of Curtice-Burns. The current work force of 140 persons will be retained and operations wil be maintained substantially as in the past, according to David J. McDonald, Curtice-Burns president.

Refrigeration Engineering Corp.: Brenda Kerlick has joined this San Antonio-based firm as electrical designer. Her responsibilities include the design of electrical control systems for RECO's industrial refrigeration packaged systems.

Design Systems, Inc.: William R. Horton, former Pepsi Cola executive, has been named executive vice president and chief operating officer of this Auburn, Washington, equipment designer and manufacturer. The announcement was made by David Pratt, Design Systems president.

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The Use of Oxygen Scavengers to Prevent the Transient Discolouration of Ground Beef Packaged Under Controlled, Oxygen-depleted Atmospheres

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ABSTRACT

Rates of O_2 absorption from air were determined for a type of commercial O_2 scavenger that is formulated for rapid O_2 absorption at chiller temperatures. Rates of O_2 absorption from N_2 atmospheres containing 600 ppm *O_2 were determined for trays that each contained* 350 g *of ground beef. Packs with controlled atmospheres of N_2 that contained ground beef and O_2 scavengers were prepared, to determine the conditions under which the scavengers could prevent the transient discolouration of the meat which arises from its reaction with the residual O_2 initially present in pack atmospheres.*

The rates of O_2 absorption by individual scavengers varied from the average by ±50%. *The rate of O_2 absorption declined with decreasing oxygen concentration, from an average value per scavenger of about* 12 ml h^{-1} *when O_2 concentrations were between* 20 *and* 10%. *At O_2 concentrations* < 1% (10,000 ppm) *the rate of O_2 absorption was directly proportioned to the O_2 concentration so that the O_2 concentration in an atmosphere in a gas-impermeable pouch declined exponentially with time. The absorption of O_2 by ground beef was similarly dependent on the O_2 concentration. At* 2°C, *the transient discolouration of beef in atmospheres initially containing about* 50 ppm *O_2 was prevented by the presence of* 17·5 *scavengers per l of atmosphere. At* −1·5°C, *discolouration was prevented by* 5 *scavengers per l. The findings indicate that the O_2 concentration in pack atmospheres has to be reduced below* 10 ppm *within* 30 min *at* 2°C.

Contribution No: 778 Agriculture Canada Research Station, Lacombe, Alberta.
Contribution No: 28 Western Canadian Research Group on Extended Storage of Meats and Meat Products.

or 2 h at −1·5°C if ground beef is not to transiently discolour. It is unlikely that the required rates of O_2 absorption could be obtained economically with currently available, commercial O_2 scavengers.

INTRODUCTION

The storage life of chilled meat can be extended by packaging the product under controlled atmospheres of N_2 or CO_2 (Gill and Molin, 1991). When first established, such controlled atmospheres will contain low concentrations of O_2 (Gill, 1989). During the first few days of storage the residual O_2 is removed from the atmospheres by reactions with the meat, which include the formation of metmyoglobin (Gill and Jones, 1994*a*). The brown metmyoglobin formed at the meat surface can dull and discolour the meat but, if the amount of O_2 is not excessive, the metmyoglobin reduction activity of the muscle tissue will subsequently reduce the metmyoglobin to deoxymyoglobin and the meat will develop a desirable appearance when it is exposed to air (Ledward, 1985).

The occurrence and the duration of transient discolouration are affected by the concentration and quantity of O_2 to which the meat is exposed, the storage temperature and the intrinsic colour stability of the muscle tissue. When stored at −1·5°C, muscle of relatively high intrinsic colour stability, such as beef *longissimus dorsi*, will not discolour in atmospheres of 1 to 2 *l* kg^{-1} of meat that contain several hundred ppm O_2, but will discolour in atmospheres containing < 100 ppm O_2 when stored at 2°C. Products of low colour stability, such as ground beef, will discolour when O_2 concentrations are < 100 ppm irrespective of the storage temperature (Gill and McGinnis, 1995).

The discolouration induced by the residual oxygen in controlled atmospheres will resolve after 2 to 4 days (Gill and Jones, 1994*a*,*b*). That transient discolouration is then of no consequence when the meat will consistently be stored for lengthy periods. However, the discolouration would be inconvenient in circumstances where some portion of the meat might be displayed shortly after being packaged. Such circumstances could arise in operations for the central preparation of display-ready beef (Farris *et al.*, 1991). Some means of preventing the transient discolouration would then remove a restriction on the use of O_2-depleted atmospheres to preserve display-ready beef in master packagings.

An obvious approach to preventing the discolouration is to include an O_2 scavenging system in the master pack, and so sequester most of the residual O_2 from the meat (Rousset and Renerre, 1991). Oxygen scavengers for use with foods are commercially available, but the information on their scavenging behaviour is limited, and essentially non-existent for their rates of reaction with O_2 at concentrations of < 1000 ppm. Nor is much information available on the rate of O_2 uptake by meat at those low O_2 concentrations. The uptakes of O_2 from controlled atmospheres of N_2 by a type of commercial oxygen scavenger and by ground beef, and the prevention of transient meat discolouration by the inclusion of O_2 scavengers with ground beef packaged under N_2 were therefore examined, to identify the amount of scavenging activity that would be required to prevent the transient discolouration of meat when it is packaged under an O_2-depleted atmosphere.

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MATERIALS AND METHODS

Oxygen scavengers

The O_2 scavengers used in this study (FreshPax™ 200R; Multiform Desiccants Inc., Buffalo, NY, U.S.A.) are composed of an iron-based chemical system which is packaged in a pouch of a spunbonded polyolefin film (Tyvek™). That film is highly permeable to gasses and water vapour, damage resistant and food compatible. The R-type scavenging system is formulated for activity at chiller temperatures with dry foods. The rated capacity of each scavenger is 200 ml of O_2.

Measurement of O_2 concentrations

The concentrations of O_2 in atmospheres were determined using an O_2 analyzer (Mocon MS-750; Modern Controls Inc., Minneapolis, MN, U.S.A.) that employs a zirconium oxide sensor. A gas sample of 10 ml, withdrawn from a test atmosphere into a gas-tight syringe, was injected into the sensor for each determination of O_2 concentration.

Uptake of O_2 by scavengers from atmospheres of air

Ten scavengers were each sealed into a pouch composed of a gas impermeable, bimetalized, plastic laminate (SecureFresh Pacific Ltd., Auckland, New Zealand) containing approximately 250 ml of air. The filled pouches were held at 20 ± 1°C. Immediately after the closure of each pouch, and after storage of each for 1 h, two samples of each pouch atmosphere were withdrawn, through a stick-on septum, for analysis. After the removal of the first pair of samples, the pierced area of a pouch was sealed using a hot iron. After the final sampling, the volume of the atmosphere remaining in each pack was determined by removing the atmosphere with a syringe. The volume of O_2 absorbed by each scavenger was estimated from the measured O_2 concentrations and the calculated volume of the atmosphere at the beginning of the storage period.

Ten pouches of the gas-impermeable laminate were each filled with 32 scavengers and 4 *l* of air. Duplicate pouches were stored at temperatures of −1·5, 2, 10, 20 or 30°C. The scavengers that were placed in each pouch had been held overnight at the temperature at which the pouch was to be stored. At hourly intervals for up to 10 h, the O_2 concentration of each pouch atmosphere was determined, with duplicate samples being withdrawn through a stick-on septum, and sealing of the punctured area after each sampling.

Uptake of O_2 from N_2 atmospheres by ground beef

Eight pouches of the gas-impermeable laminate were each filled with four trays of ground beef and 4 *l* of N_2. The pouches were evacuated, gassed and sealed using a Captron III (RMF Inc., Grandview, MO, U.S.A.) controlled atmosphere packaging machine. Each pouch was injected with 10 ml of air, to increase the oxygen concentration in the pack atmosphere to about 600 ppm. The punctured area of each pouch was sealed immediately after injection of the air. Duplicate pouches

were stored at −1·5, 2, 5 or 10°C, and the O_2 concentration of each atmosphere was determined as for the 4 *l*, air-filled pouches containing scavengers.

The ground beef for each pair of pouches was prepared from 3 kg of lean beef trimmings that had been stored overnight at the intended temperature of storage of the ground beef. The trimmings were ground immediately after their removal from storage, well mixed by hand, then distributed into eight solid polystyrene trays. The tray dimensions were 220 × 140 × 25 mm. Each tray was filled with 350 g of ground beef; which was pressed into the tray to give a firm meat mass with a smooth surface. Each tray was overwrapped with a stretch film (Vitafilm Choice Wrap, Goodyear Canada, Inc., Toronto, ON) that has an O_2 transmission rate of about 8000 ml m^{-2} atm^{-1} 24 h^{-1} at 25°C and 75% r.h. Two holes each approximately 0·5 mm in diameter, were made in the upper surface of the film at diagonally opposite corners of each tray. Those vents in the display trays assured that pressure differences between the inside and the outside of trays did not develop during the evacuation and gassing of master packs, and so avoided bursting or collapse of the display trays. The times between removal of the trimmings from storage and the return of the packaged ground beef to storage did not exceed 30 min.

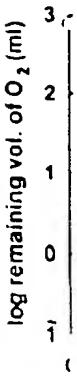
Preservation of ground beef colour by O_2 scavengers

Pouches containing trays of ground beef under N_2 atmospheres were prepared as before, but without air being injected into the pouches after they were sealed. In addition to the meat, the duplicate pouches contained 0, 10, 20, 30, 40, 50, 60, 70 or 80 O_2 scavengers, and were stored at either −1·5 or 2°C for 24 h. The O_2 concentration in each pouch atmosphere was determined immediately after the pouch was sealed and immediately before it was opened.

After storage, the trays were removed from the pouches and placed in a refrigerated display case. The meat was allowed 1 h to bloom in air, then the meat in each tray was assessed, for retail acceptability and discolouration, by a five member panel. Retail acceptability was scored on a 7-point scale where 1 = extremely undesirable, 2 = undesirable, 3 = slightly undesirable, 4 = neither desirable nor undesirable, 5 = slightly desirable, 6 = desirable, and 7 = extremely desirable. Discolouration was scored on a 5- point scale where 1 = no discolouration, 2 = 1-10% discolouration, 3 = 11–25% discolouration, 4 = 26–50% discolouration, and 5 = 51–100% discolouration. The scores assigned to each tray of meat by the majority of the panelists were recorded.

RESULTS AND DISCUSSION

Commercial O_2 scavengers are based on iron powders ('activated iron oxide') which are mixed with acids and/or salts and a humectant, to promote oxidation of the iron (Idol, 1987). The humectant may be dry or pre-wetted. If the humectant is dry, the rate of O_2 absorption by the scavenger will increase until sufficient water has been absorbed from a moist atmosphere to allow O_2 absorption at the maximum rate. If the humectant is moist, as in the scavengers used for this study, O_2 absorption will proceed at a near-maximum rate when the scavenger is exposed to an aerobic atmosphere.



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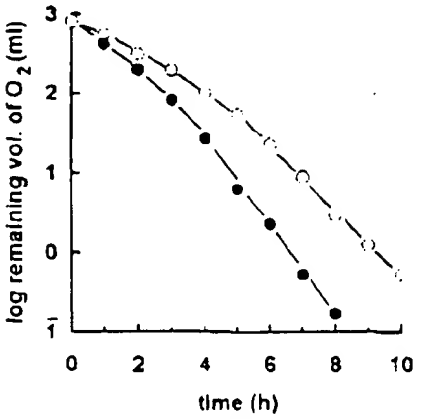

Fig. 1. The effects of time in storage at 1·5°C (○) or 20°C (●) on the volumes of O_2 in packs filled with 4 *l* of air and 32 O_2 scavengers. Plotted values are the averages for duplicate packs.

The manufacturers' literature that describes the behaviour of commercial O_2 scavengers indicates that they are generally formulated to reduce the O_2 concentration in a volume of air that is 5 times the rated O_2 absorbing capacity of the scavenger to < 100 ppm within about a day, but that the time taken to reach that value may vary from 0·5 to 4 d (Smith *et al.*, 1986; Multiform Desiccants, 1992). That variation is due apparently in part to different rates of O_2 absorption by the individual scavengers, of the same type, as the volumes of O_2 absorbed from air by individual scavengers, at 20°C, during the first hour after the closure of packs ranged from 7·4 to 16·9 ml, and averaged 10·8 ml for the 10 scavengers examined. Thus, a consistent rate of O_2 absorption could be expected only when pouches contain several O_2 scavengers, so that the total rate of absorption approximates the value that would be estimated from the average rate of absorption and the number of scavengers used, while 3 or more scavengers l^{-1} of air would be required to achieve low O_2 concentrations in about 8 h.

In packs that contained 32 scavengers, and 4 *l* of air, the rates of O_2 absorption declined with time, the decline being exponential after the residual O_2 fell below about 50 ml; i.e. when O_2 concentration were < 1% (Fig. 1). Those data suggest that the rate of O_2 absorption is affected by a number of factors which include the O_2 concentration. When the residual O_2 was > 400 ml; i.e. at O_2 concentrations > 10%, the O_2 concentration apparently had a relatively minor effect upon the rate. The effect of O_2 concentration increasingly predominated as it decreased below 10% until, at concentrations < 1%, the rate of O_2 absorption was directly related to the O_2 concentration. Rates of O_2 absorption from pack atmospheres containing < 1% (10,000 ppm) O_2 can then be conveniently expressed by the half-life of O_2 in the atmospheres, the O_2 half-life being the time required to reduce by half any initial volume, or concentration, of residual O_2.

The volumes of O_2 absorbed by 32 scavengers during the first hour, when O_2 concentrations remained > 10%, increased with the storage temperature for temperatures of −1·5, 2 and 10°C, but did not increase further at higher temperatures (Table 1). Similarly, the half-life of O_2 in the atmospheres, when

TABLE 1

The Effect of Storage Temperature on the Volumes of O_2 Absorbed During the First Hour, When the O_2 Concentration Remained >10%, and on the Half Life of O_2, When the O_2 Concentration was <1%, for Packs Filled with 32 O_2 Scavengers and 4 *l* of Air. The Values are the Averages for Duplicate Packs

Temperature (°C)	*O_2 absorbed during the first h (ml)*	*1/2-life of O_2 when $[O_2]$ < 1% (h)*
−1·5	262	0·63
2	283	0·56
10	384	0·50
20	388	0·50
30	366	0·52

the O_2 concentration was <1%, decreased with increasing storage temperatures at temperatures <10°C, but did not decrease further at higher temperatures. The average volume of O_2 absorbed per scavenger during the first hour of storage at 10°C or higher temperatures was about 12 ml, a value that is comparable with the average volume observed to be absorbed by single scavengers at 20°C. For a scavenger of average activity in an atmosphere of 1 *l* containing <1% O_2, the half-life of O_2 at storage temperatures of −1·5, 2 and 10°C would be 5·0, 4·5 and 4·0 h respectively, those half-lives being 8 times the half-lives of O_2 in the packs which contained 4 *l* of gas and 32 scavengers. The relatively small effect of temperature on the rate of O_2 absorption would be an expected result of the scavengers having been formulated for high rates of O_2 absorption at chiller temperatures. Rates of O_2 absorption by scavengers of other types might vary more with temperature.

The absorption of O_2 by ground beef from atmospheres containing ≤600 ppm of O_2 also decreased exponentially with time. The half-life of O_2 declined with increased storage temperature for temperatures between −1·5 and 5°C, but the half-life at 10°C was similar to that at 5°C (Table 2). For trays of ground beef in atmosphere volumes of 1 *l* per tray, the half-life of O_2 increased, from a value of 1·5 h, by about 0·4 h $°C^{-1}$ for temperatures below 5°C.

TABLE 2

The Effect of Storage Temperature on the Half-Life of O_2 in Packs Containing Four Trays of Ground Beef and 4 *l* of N_2 Contaminated with 600 ppm O_2. The Values are the Averages for Duplicate Packs

Temperature (°C)	*1/2-life of O_2 (h)*
−1·5	4·7
0	3·8
2	2·9
5	1·4
10	1·6

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between the rate of O_2 abso
described by the limited data
order of the rate of O_2 abs
absorption is likely to decre
temperature range.

The N_2 atmosphere first e
beef contained O_2 at conc
degradation of meat colour
the meat unacceptable, but
with freshly ground product
their customers. The inclus
resulted in the meat being of
packs were opened after sto
scavengers l^{-1} of atmospher
temperature was also judged
of small areas of brown dis
packs were stored at 2°C,
discolouration and degradat
centrations of residual O_2 in
either temperature for 24 h

The Initial and Final O_2 Con
Retail Acceptability and Disco
for 24 h, at 1·5 or 2°C, With or
Concentrations are the Averag
Favourable of the Scores Reco

Temperature (°C)	*No. of scavengers*
−1·5	0
	10
	20
2	0
	60
	70

Retail acceptability: 1 = extren
4 = neither desirable or undes
desirable.
Discolouration: 1 = no disco
colouration, 4 = 26-50% disc

es of O_2 Absorbed During the First
%, and on the Half Life of O_2, When
with 32 O_2 Scavengers and 4 *l* of Air.
r Duplicate Packs

	1/2-life of O_2 when $[O_2] < 1\%$ (h)
	0·63
	0·56
	0·50
	0·50
	0·52

:h increasing storage temperatures
urther at higher temperatures. The
during the first hour of storage at
ı value that is comparable with the
single scavengers at 20°C. For a
e of 1 *l* containing < 1% O_2, the
2 and 10°C would be 5·0, 4·5 and
:s the half-lives of O_2 in the packs
rs. The relatively small effect of
d be an expected result of the sca-
s of O_2 absorption at chiller tem-
rs of other types might vary more

ıtmospheres containing ≤600 ppm
The half-life of O_2 declined with
:s between −1·5 and 5°C, but the
ble 2). For trays of ground beef in
e of O_2 increased, from a value of
ow 5°C.

of O_2 in Packs Containing Four Trays
th 600 ppm O_2. The Values are the
:e Packs

1/2-life of O_2 (h)
4·7
3·8
2·9
1·4
1·6

The rate of O_2 absorption by meat is highly variable (Ledward, 1970; Hood, 1980). O_2 absorption by post-rigor muscle is not affected by the degree of comminution of the tissue (Bendall and Taylor, 1972), while grinding, mixing and forming unit masses with the same surface area would tend to reduce the variation between units prepared from the same batch. However, separate batches of meat were used for determining the rate of O_2 absorption at each temperature, without determination of the variation between batches. The relationship between the rate of O_2 absorption and temperature may then not be wholely as described by the limited data. Despite that, the data seem sufficient to indicate the order of the rate of O_2 absorption by the ground beef, and that the rate of O_2 absorption is likely to decrease substantially with temperature within the chiller temperature range.

The N_2 atmosphere first established in controlled atmosphere packs of ground beef contained O_2 at concentrations between 40 and 50 ppm (Table 3). The degradation of meat colour at those very low O_2 concentrations did not render the meat unacceptable, but the affected product would certainly compare poorly with freshly ground product, which would then be preferred by both retailers and their customers. The inclusion in the packs of 5 scavengers l^{-1} of atmosphere resulted in the meat being of desirable appearance, and not discoloured, when the packs were opened after storage for 24 h at −1·5°C. Meat from packs with 2·5 scavengers l^{-1} of atmosphere which were stored for the same time at the same temperature was also judged to be of desirable appearance despite the occurrence of small areas of brown discolouration on the meat in most of the trays. When packs were stored at 2°C, 17·5 scavengers l^{-1} were required to wholely prevent discolouration and degradation of the appearance to slightly desirable. The concentrations of residual O_2 in the packs, with or without O_2 scavengers, stored at either temperature for 24 h were ≤11 ppm.

TABLE 3

The Initial and Final O_2 Concentrations in Pack Atmospheres, and the Scores for the Retail Acceptability and Discolouration of Trays of Ground Beef Stored Under 4 *l* of N_2 for 24 h, at −1·5 or 2°C, With or Without O_2 Scavengers Being Included in the Packs. The O_2 Concentrations are the Averages for Two Packs. The Organoleptic Scores are the Least Favourable of the Scores Recorded for Each of the Eight Trays Removed from Two Packs

Temperature (°C)	*No. of scavengers*	*$[O_2]$ (ppm)*		*Retail acceptability*	*Discolouration*
		initial	*final*		
1·5	0	40	11	5	3
	10	43	8	6	2
	20	49	10	6	1
2	0	54	10	5	4
	60	41	8	5	2
	70	49	7	6	1

Retail acceptability: 1 = extremely undesirable, 2 = undesirable, 3 = slightly undesirable, 4 = neither desirable or undesirable, 5 = slightly desirable, 6 = desirable, 7 = extremely desirable.
Discolouration: 1 = no discolouration, 2 = 1–10% discolouration, 3 = 11–25% discolouration, 4 = 26–50% discolouration, 5 = 51–100% discolouration.

As the sensitivity of the oxygen analyzer is 10 ppm, the final values for O_2 concentrations indicate only that the O_2 concentrations were in the range 10 to 0 ppm. The times required to reduce the O_2 concentration from 50 to < 10 ppm would be little more than twice the half-life of the O_2 in a pouch atmosphere. With the number of scavengers required to prevent the discolouration of ground beef at 2°C, the half-life of O_2 would be 0·26 h. The meat would contribute < 10% to the total O_2 absorbing activity within the pouch. Thus meat discolouration at 2°C is prevented when the residual O_2 in the atmosphere is reduced to < 10 ppm within 30 min of pouch closure. With the number of scavengers required to prevent the discolouration of beef at −1·5°C, the half-life of O_2 would be somewhat more than 1 h, but the meat would contribute about 20% to the total O_2 absorbing activity. Thus, at −1·5°C, meat discolouration is prevented when the residual O_2 in the atmosphere is reduced to < 10 ppm within 2 h of pouch closure.

Obviously, each doubling of the initial O_2 concentration from any base value would require the O_2 absorbing capacity to be increased by an increment equal to the absorbing capacity needed to prevent discolouration at the base concentration, if discolouration at the higher concentrations was to be prevented. Also, the O_2 absorbing capacity required to prevent discolouration would vary directly with the volume of the atmosphere.

Although the rate of metmyoglobin formation at muscle tissue surfaces is reported to be maximal at about 6000 ppm O_2 (Ledward, 1970), it is evident from this study that meat colour can degrade rapidly at O_2 concentrations < 100 ppm. With that rapid deterioration, currently available, commercial, O_2 scavengers would probably have to be used in multiple numbers per display pack to consistently prevent the transient discolouration of meat that is packaged under O_2-depleted atmospheres. However, the number of scavengers required would be minimized if packaging conditions could be adjusted to assure that meat temperatures would be ≤ −1°C, that the pack atmosphere would initially contain < 100 ppm O_2 and that the volume of the pack atmosphere would be small in comparison with the weight of meat in the pack.

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FOOD MICROBIOLOGY AND FOOD SAFETY INTO THE NEXT MILLENNIUM

(2)

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misinterpreted in the absence of storage trials or in trials of short duration such as 14 days. If *Brochothrix thermosphacta* is a problem organism in a processing facility or on a particular type of meat, lysozyme, Chrisin or mixtures of the two could be used to control its growth during refrigerated anoxic storage.

PACKAGING OF GROUND BEEF IN AN ATMOSPHERE WITH LOW CARBON MONOXIDE AND HIGH CARBON DIOXIDE RESTRAINS GROWTH OF *ESCHERICHIA COLI* O157:H7, *LISTERIA MONOCYTOGENES, YERSINIA ENTEROCOLITICA* AND *SALMONELLA DIARIZONAE*

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Ground beef for retail sale is most often ready packed in modified atmosphere (MA) or in chub packs. MA packed ground beef prolongs the microbiological shelf life and also maintains an attractive red colour. For the past decade the Norwegian meat industry has been using a gas mixture of 0.3-0.5% CO, 60-70% CO_2 and 30-40% N_2 (the CO comes ready mixed in the N_2). The reason for adding CO to the gas mixture is that it will produce a long-lasting cherry-red colour of the meat (Sørheim et al 1999). The most commonly used gas mixture for retail-ready meat in other European countries is 70% O_2/30% CO_2 (Gill 1996). The high oxygen concentration is needed to keep the red colour of the meat. It is therefore only possible to obtain half the CO_2 concentration used in the CO gas mixture. The microbiological shelf life will be longer than in air, but less than in the CO gas mixture (Sørheim et al 1999).

The inclusion of CO is controversial because the stable cherry –red colour can last beyond the microbiological shelf life of the meat and thus mask spoilage (Kropf 1980). However, the consumer is able to evaluate the microbiological conditions of the meat by off-odours and the shelf life based on odour is significantly longer in the CO mixture only at 4°C. Thus, extended shelf life does not necessarily imply an increased risk of growth of pathogens. In the present study we wanted to compare growth of the pathogens *Escherichia coli* O157:H7, *Listeria monocytogenes, Yersinia enterocolitica* and *Salmonella diarizonae,* in ground beef packed in a commercial Norwegian 0.4% CO/60% CO_2/40% N_2 mixture with growth in a high O_2 (70% O_2/30% CO_2) gas mixture and in ground beef in chub packs during storage at 4 and 10°C.

Commercial packages of ground beef (500 g) stored at 10°C were inoculated with the pathogens *Escherichia coli* O157:H7, *L. monocytogenes, Y. entercolitca* and *S.*

diarizona, and the ground beef stored at 4°C with *L. monocytogenes* and *Y. enterocolitica*. The inocula of *L. monocytogenes* and *Y.* enterocolitica were cocktails of 3 stationary-phase, rifampicin-resistant strains, the inoculum of *E. coli* O157:H7 was one non-toxic nalidixic/streptomycin resistant strain and that of *S. diarizonae* was a cocktail of 3 strains that were not made antibiotic resistant (plated on selective media for *Salmonella* spp.). Controls of ground beef without inoculated pathogens were stored at both temperatures.

After 5 days storage at 10°C the ground beef packed in the CO mixture had an acceptable smell while beef the packed in the high O_2 mixture and the chub packs had a slight off-odour. After 8 days storage there was a strong off-odour for all the treatments. At 4°C the smell was still acceptable after 14 days of storage in the CO mixture, but the high O_2 mixture and the chub packs had some off-odours. The growth of pathogens was restrained in all samples that had been packed in the gas mixture containing CO. Thus, growth of *Y. enterocolitica* was nearly totally inhibited both at 4 and 10°C, while the number in the samples packed in the high O_2 mixture increased from about $5x10^2$ bacteria per g at day 0 to about 10^4 at day 5 at 4°C and to 10^5 at 10°C. The number in the chub packs were even higher. *L. monocytogens* showed very little growth at 4°C in all of the treatments. At 10°C there was slow growth (from about $5x10^3$ bacteria/g to about 10^4 at day 5) in the CO mixture while the number in the high O_2 mixture and the chub packs were about 10 times higher. Growth of *E. coli* O157:H7 at 10°C storage was slow both in the CO-mixture and the high O_2 mixture. Growth in the chub packs was higher reaching 10^5 bacteria/g on day 5. The growth of *S. diarizonae* followed the same pattern as *E. coli* O157:H7.

Ground beef is a high-risk product because pathogens may be mixed into the product which may not be properly heated before being eaten. The present study shows that the reduced background flora of beef packed in the CO mixture did not result in increased growth of the pathogens. This was probably due to the high concentration of CO_2 in this mixture which particularly inhibits Gram negative bacteria. The O_2 content in the CO mixture was virtually zero throughout storage at both temperatures. At 10°C the O_2 content in the high O_2 gas mixture decreased from 70% to about 35% after 8 days, probably due to aerobic bacterial metabolism. The chub packs had air- permeable casing which probably was the cause of the high bacterial growth in these packs.

The conclusion of the present study is that for the conditions studied, the risk of growth of the pathogens *Y. entrocolitica, L. monocytogenes, E. coli* O157:H7 and *S. diarizonae* in ground beef stored in CO gas mixture is the same as or less than in the ground beef stored in high O_2 or under vacuum (chub packs).

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English summary

(3)

CONSUMER PURCHASE PROBABILITY OF BEEF AND PORK PACKAGED IN DIFFERENT ATMOSPHERES

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Ground beef, beef loin steaks and pork chops were packaged in modified atmospheres of 0.4% CO/ 60% CO_2/ 40% N_2 (high CO_2/low CO mixture) and 70% O_2/ 30% CO_2 (high O_2 mixture). In addition ground beef was packaged in clipped chub packs, beef loin steaks were vacuum packaged, and pork chops were packaged in an atmosphere of 60% CO_2/ 40% N_2 with each pack containing an O_2 absorber. The purchase probability data were collected by interviewing 126 consumers usually purchasing meat and meat products. The consumers visually compared the samples within each type of meat. The consumers preferred ground beef packaged in the high CO_2/low CO mixture or the high O_2 mixture compared to ground beef packaged in clipped chub packs. Purchase probability increased when pork chops were packaged in the high CO_2/low CO mixture. Pork chops in packs containing an O_2 absorber, were rated lowest in purchase probabilities. The purchase probability for beef loin steaks was similar when packaged in the high CO2/low CO mixture or the high O2 mixture, and these products were preferred compared to beef loin steaks packaged in vacuum.

COMMISSIONED REPORT

MATFORSK – Norwegian Food Research Institute

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Report No.:
O-7224
Availability: Confidential

Report Title: Consumer Survey of Meat Products	**Date:** July 11, 1996
Project Manager/Author: Ragnhild Solheim	**Signature of Project Manager:** [Signature]
Head of Department: Bjørg Egelandsdal	**Signature of Head of Department:** [Signature]
Department: Analysis Methodology	**Project No:** O-7224 FBT
Commissioned by: Norsk Kjøtt [Norwegian Meat]	**Commissioner's contact:** Truls Nesbakken

OPPDRAGSRAPPORT

MATFORSK - Norsk institutt for næringsmiddelforskning

Osloveien 1, 1430 Ås
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Rapportnummer:
O-7224
Tilgjengelighet: Fortrolig

Rapportens tittel: Forbrukertest av kjøttvarer	**Dato:** 11.07.96
Prosjektleder/forfatter: Ragnhild Solheim	**Prosjektleders signatur:** Ragnhild Solheim
Avdelingsleder: Bjørg Egelandsdal	**Avdelingsleders signatur:** Bjørg Egelandsdal
Avdeling: Analysemetodikk	**Prosjektnummer:** O-7224 FBT
Oppdragsgiver: Norsk Kjøtt	**Oppdragsgivers ref:** Truls Nesbakken

Summary/Abstract:

The consumers' (N=126) purchasing tendency for ground meat, pork chops and top loin of beef packaged in various ways was measured by means of a central location test. The consumers indicated their purchasing tendency on a verbal five-point scale from "Will definitely not buy" to "Will definitely buy." Moreover, the consumers estimated their buying frequency for the three different products, and provided their age and gender.

The consumer population was composed of 62 % women and 38 % men. The age distribution was roughly equivalent for both genders.

Purchasing Frequency:
The major segment (47.6 %) of the participants said that they buy ground meat two to three times a month, while 20.6 % buy ground meat once a month.

Pork chops were purchased two to three times a month by 29.4 % of the participants, while 38.1 % bought pork chops once a month. 29 % of the participants bought pork chops less frequently than once a month.

Top loin was purchased less frequently than once a month by 58.1 % of the participants in the study. 18 % said that they buy top loin once a month, and 19.4 % indicated that they buy top loin once a week.

Purchasing Tendency:
Ground meat: Ground meat packaged with CO gas received the same average score for purchasing tendency as ground meat packaged in O_2 gas, while ground meat packaged as sausage had the lowest score for purchasing tendency.

Pork Chops: Pork chops packaged in CO gas received the highest total score for purchasing tendency, while pork chops packaged in O_2 gas received the second highest total score and pork chops packaged with oxygen absorber received the lowest score.

Top Loin: Top loin packaged in CO gas and in O_2 gas had roughly the same average score for purchasing tendency, while vacuum-packaged top loin received the lowest score for purchasing tendency.

Sammendrag/ekstrakt:

Forbrukeres (N = 126) kjøpsintensjon for kjøttdeig, svinekoteletter og ytrefilet av storfe emballert på ulike måter ble målt ved en "central-location" test. Forbrukerne anga kjøpsintensjon etter en verbal fem-punkts skala fra "Vil sikkert ikke kjøpe" til "Vil sikkert kjøpe". I tillegg anslo de kjøpsfrekvens for de tre ulike varetypene, samt oppga alder og kjønn.

Forbrukerutvalget besto av 62 % kvinner og 38 % menn med en relativt jevn aldersfordeling.

Kjøpsfrekvens:
Hovedtyngden (47.6 %) av deltakerne sa at de kjøper kjøttdeig to - tre ganger pr måned, mens 20.6 % kjøper kjøttdeig en gang pr måned.

Svinekoteletter ble kjøpt to - tre ganger pr måned av 29.4 % av deltakerne, mens 38.1 % kjøpte svinekoteletter en gang pr måned. 29 % av deltakerne kjøpte svinekoteletter sjeldnere enn en gang pr måned.

Ytrefilet ble kjøpt sjeldnere enn en gang pr måned av 58.1 % av de som deltok i testen. 18 % sa at de kjøper ytrefilet en gang pr måned, og 19.4 % sa at de kjøper ytrefilet en gang pr uke.

Kjøpsintensjon:
Kjøttdeig: Kjøttdeig pakket i CO-gass og kjøttdeig pakket i O_2-atmosfære fikk samme gjennomsnittpoeng for kjøpsintensjon, mens kjøttdeig pakket som snabb fikk lavest poeng for kjøpsintensjon.

Svinekoteletter: Svinekoteletter pakket i CO-atmosfære fikk høyest poeng for kjøpsintensjon, svinekoteletter pakket i O_2-atmosfære fikk nest høyest poeng og svinekoteletter pakket med oksygen absorber fikk lavest poeng.

Ytrefilet: Ytrefilet pakket i CO-gass og i O_2-gass fikk omtrent samme gjennomsnittlig poeng for kjøpsintensjon, og vakumpakket ytrefilet fikk lavest poeng for kjøpsintensjon.

MATFORSK – Norwegian Food Research Institute

Table of Contents

Innhold

1. Premise

The consumers' choice of meat products may be attributed to factors such as how the products are presented in their packaging. The consumers' purchasing tendency for meat products packaged in accordance with various principles was therefore measured.

2. Implementation

2.1 Materials and Survey Conditions

The survey was taken at Drøbak City [shopping center] on June 12, 1996 (Tuesday) from 10 am to 4 pm.

Ground meat, pork chops and top loin of beef packaged in accordance with various principles (Table 1) was presented to consumers who eat these types of products. The products were delivered to MATFORSK on June 8, 1996 and stored at 4°C until the survey date.
Products from the same group were placed side by side on a table under lighting with a strength of approximately 2000 lux (equivalent to the light intensity of a refrigerated meat counter in a store). The products were replaced with cold stored products every three hours.

Table 1. *Packaging methods for meat products tested in consumer survey*

Meat Product		Packaging Method			
	Sausage	CO	O_2	Vacuum	O_2 w/absorber
Ground Meat	x	x	x		
Pork Chops		x	x		x
Top loin of beef		x	x	x	

x = packaging method used

2.2 Method

The products were coded with three-digit random numbers and evaluated in a systematically rotating order. The consumers indicated purchasing probability on a verbal scale and purchasing frequency for the product, and gave their age and gender (Figure 1). Following the evaluation, the verbal scale was translated into numerical values from 1 to 5, where 1=Will definitely not buy, and 5=Will definitely buy. The consumers spent between 5 and 10 minutes answering the questions.

1. Problemstilling

Forbrukernes kjøp av kjøttvarer kan blant annet ha sammenheng med hvordan varene presenteres i emballasjen. Forbrukernes kjøpsintensjon av kjøttvarer emballert etter ulike prinsipper ble derfor målt.

2. Gjennomføring

2.1 Materialer & testforhold

Testen ble gjennomført på Drøbak City den 12.06.96 (tirsdag) fra kl 1000 - 1600.

Kjøttdeig, svinekoteletter og ytrefilet av storfe emballert etter ulike prinsipper (Tabell 1) ble presentert for forbrukere som spiser disse produkttypene. Produktene ble levert MATFORSK den 08.06.96, og ble oppbevart ved 4 °C til testdato. Produkter fra samme gruppe ble plassert ved siden av hverandre på et bord ved belysning på ca 2000 lux (tilsvarende lysintensitet i kjøledisk i butikk). Produktene ble skiftet ut med kjølelagret vare hver tredje time.

***Tabell 1.** Pakkemetoder for kjøttvarer testet ved forbrukertest*

Kjøttvare		**Pakkemetode**			
	Snabb	CO	O_2	Vakuum	O_2 m/absorber
Kjøttdeig	x	x	x		
Svinekoteletter		x	x		x
Ytrefilet av storfe		x	x	x	

x = anvendt pakkemetode

2.2 Metode

Produktene ble kodet med tresifrete tilfeldige tall og vurdert i systematisk roterende rekkefølge. Forbrukerne anga kjøpssannsynlighet etter en verbal skala, kjøpsfrekvens for produktet samt alder og kjønn (Figur 1). Den verbale skalaen ble etter vurderingen oversatt til tallverdier fra 1 til 5, hvor 1 = Vil helt sikkert ikke kjøpe, opptil 5 = Vil helt sikkert kjøpe. Forbrukerne brukte mellom 5 og 10 minutter på å besvare spørsmålene.

MATFORSK – Norwegian Food Research Institute

Dear Consumer!
We are taking a survey on the consumer opinion concerning a selection of meat products as they appear in the meat counter. We hope that you will take a minute to let the meat producers know your opinion!

What to do:
1. Please take a look at the samples of top loin.
2. Consider whether you would buy these products the way they appear, assuming they are priced the same. Evaluate the products in the order listed below and check one box for each product

Sample marked 763		**Sample marked 288**	
Will definitely buy	☐	Will definitely buy	☐
May buy	☐	May buy	☐
May/may not buy	☐	May/may not buy	☐
May not buy	☐	May not buy	☐
Will definitely not buy	☐	Will definitely not buy	☐

Sample marked 911	
Will definitely buy	☐
May buy	☐
May/may not buy	☐
May not buy	☐
Will definitely not buy	☐

In closing please answer the questions below about your age, gender and how often you buy top loin of beef.

My age (check one):

18–25 years old	☐
26–35 years old	☐
36–45 years old	☐
46–55 years old	☐
56–65 years old	☐
over 65 years old	☐

Gender (check one):
Female ☐ Male ☐

I buy top loin of beef (refrigerated):

Less than once a month	☐
Once a month	☐
Two to three times a month	☐
Once a week	☐
More than once a week	☐

THANK YOU FOR YOUR ASSISTANCE!

Figure 1. *Questionnaire for consumer survey of meat products. Corresponding forms were used for pork chops and ground meat.*

Kjære Forbruker!
Vi gjennomfører en undersøkelse av forbrukernes syn på noen utvalgte kjøttvarer slik de ser ut når vi møter dem i disken. Vi håper du tar deg tid til å bringe dine synspunkter til kjøttprodusentene!

Hva du skal gjøre:
1. Se på prøvene av ytrefilet
2. Vurdere om du tror du vil kjøpe disse produktene slik de tar seg ut, forutsatt samme pris. Vurder produktene i den rekkefølgen de er oppgitt nedenfor og sett ett kryss for hvert produkt.

Prøve merket 763
Vil sikkert kjøpe ☐
Vil kanskje kjøpe ☐
Vil kanskje/kanskje ikke kjøpe ☐
Vil kanskje ikke kjøpe ☐
Vil sikkert ikke kjøpe ☐

Prøve merket 288
Vil sikkert kjøpe ☐
Vil kanskje kjøpe ☐
Vil kanskje/kanskje ikke kjøpe ☐
Vil kanskje ikke kjøpe ☐
Vil sikkert ikke kjøpe ☐

Prøve merket 911
Vil sikkert kjøpe ☐
Vil kanskje kjøpe ☐
Vil kanskje/kanskje ikke kjøpe ☐
Vil kanskje ikke kjøpe ☐
Vil sikkert ikke kjøpe ☐

Til slutt ber vi deg besvare spørsmål om alder, kjønn og hvor ofte du kjøper ytrefilet av storfe.

Min alder er (sett ett kryss):
18-25 år ☐
26-35 år ☐
36-45 år ☐
46-55 år ☐
56-65 år ☐
over 65 år ☐

Kjønn (sett kryss):
Kvinne ☐ Mann ☐

Jeg kjøper ytrefilet av storfe (kjølevare):
Sjeldnere enn en gang pr måned ☐
En gang pr måned ☐
To - tre ganger pr måned ☐
En gang pr uke ☐
Oftere enn en gang pr uke ☐

MANGE TAKK FOR HJELPEN!

Figur 1. *Spørreskjema for forbrukertest på kjøttvarer. Tilsvarende skjema ble benyttet for svinekoteletter og kjøttdeig*

2.3 Consumer Population

124–126 consumers over 18 years of age participated in the survey of the three different meat products. There were a few more women than men among the participants, and there were fewer participants over 56 years of age than in the other age groups (Table 2). The age distribution among men and women was the same.

***Table 2**. Age and gender distribution among consumers participating in the survey.*

	No. of consumers	Gender (%)		Age (year, % distribution)					
Meat Product		Women	Men	18–25	26–35	36–45	46–55	56–65	Over 65
Ground Meat	125	61.6	38.4	15.9	19.8	18.3	20.6	11.1	14.3
Pork Chops	126	61.9	38.1	15.1	18.3	19.8	19.8	11.1	15.9
Top Loin	124	63.7	36.3	14.5	21.0	16.9	21.8	12.9	12.9

3. Results

3.1 Purchasing Frequency for Meat Products

Ground meat was most frequently bought, followed by pork chops, while top loin was rarely bought by the consumers participating in this study (Table 3). There were similar purchasing frequencies in the various age and gender groups.

***Table 3.** Purchasing Frequency for Three Different Meat Products*

	Meat Product		
Purchasing Frequency	Ground Meat (N=125)	Pork Chops (N=126)	Top Loin (N=124)
Less than once a month	11.1	29.4	58.1
Once a month	20.6	38.1	18.5
Two to three times a month	47.6	29.4	19.4
Once a week	15.1	3.2	3.2
More than once a week	5.6	0.0	0.8

3.2 Purchasing Tendency for Meat Products

A detailed overview of the purchasing tendency is provided in Attachment 1.

All differences described in the following were significant to a degree of 95 %.

2.3 Utvalg av forbrukere

124 - 126 forbrukere over 18 år deltok i testene av de tre ulike kjøttvarene. Noe flere kvinner enn menn deltok, og det var noe færre personer i gruppene over 56 år som deltok (Tabell 2). Det var tilsvarende aldersfordeling for kvinner og menn.

Tabell 2. *Alder og kjønnsfordeling av forbrukere som deltok i undersøkelsen*

	Antall	Kjønn (%)		Alder (år, %-fordeling)					
Kjøttvare	forbrukere	Kvinner	Menn	18-25	26-35	36-45	46-55	56-65	Over 65
Kjøttdeig	125	61,6	38,4	15,9	19,8	18,3	20,6	11,1	14,3
Svinekoteletter	126	61,9	38,1	15,1	18,3	19,8	19,8	11,1	15,9
Ytrefilet	124	63,7	36,3	14,5	21,0	16,9	21,8	12,9	12,9

3. Resultater

3.1 Kjøpfrekvens for kjøttvarer

Kjøttdeig ble hyppigst kjøpt, dernest svinekoteletter, mens ytrefilet ble sjelden kjøpt av forbrukerne som deltok i denne undersøkelsen (Tabell 3). Det var tilsvarende kjøpsfrekvenser innen aldersgrupper og kjønn.

Tabell 3. *Kjøpsfrekvens for tre ulike kjøttvarer*

	Kjøttvare		
Kjøpsfrekvens	Kjøttdeig (N=125)	Svinekoteletter (N=126)	Ytrefilet (N=124)
Sjeldnere enn én gang pr mnd	11,1	29,4	58,1
Én gang pr mnd	20,6	38,1	18,5
To-tre ganger pr mnd	47,6	29,4	19,4
Én gang pr uke	15,1	3,2	3,2
Oftere enn én gang pr uke	5,6	0,0	0,8

3.2 Kjøpsintensjon for kjøttvarer

Detaljert oversikt over kjøpsintensjon er gitt i vedlegg 1.

Alle forskjeller som er beskrevet nedenfor. var signifikante på 95 % nivå.

Ground Meat
Ground meat packaged as sausage was least appreciated by the consumers (see Figure 2). Ground meat packaged in CO gas and ground meat packaged in O_2 gas received the same average score for purchasing tendency. This result occurred regardless of consumer age and gender.

Comments from the consumers:
The wrapping film used to pack meat as sausage hides the contents.

[Above bar chart] **Purchasing Tendency for Ground Meat**

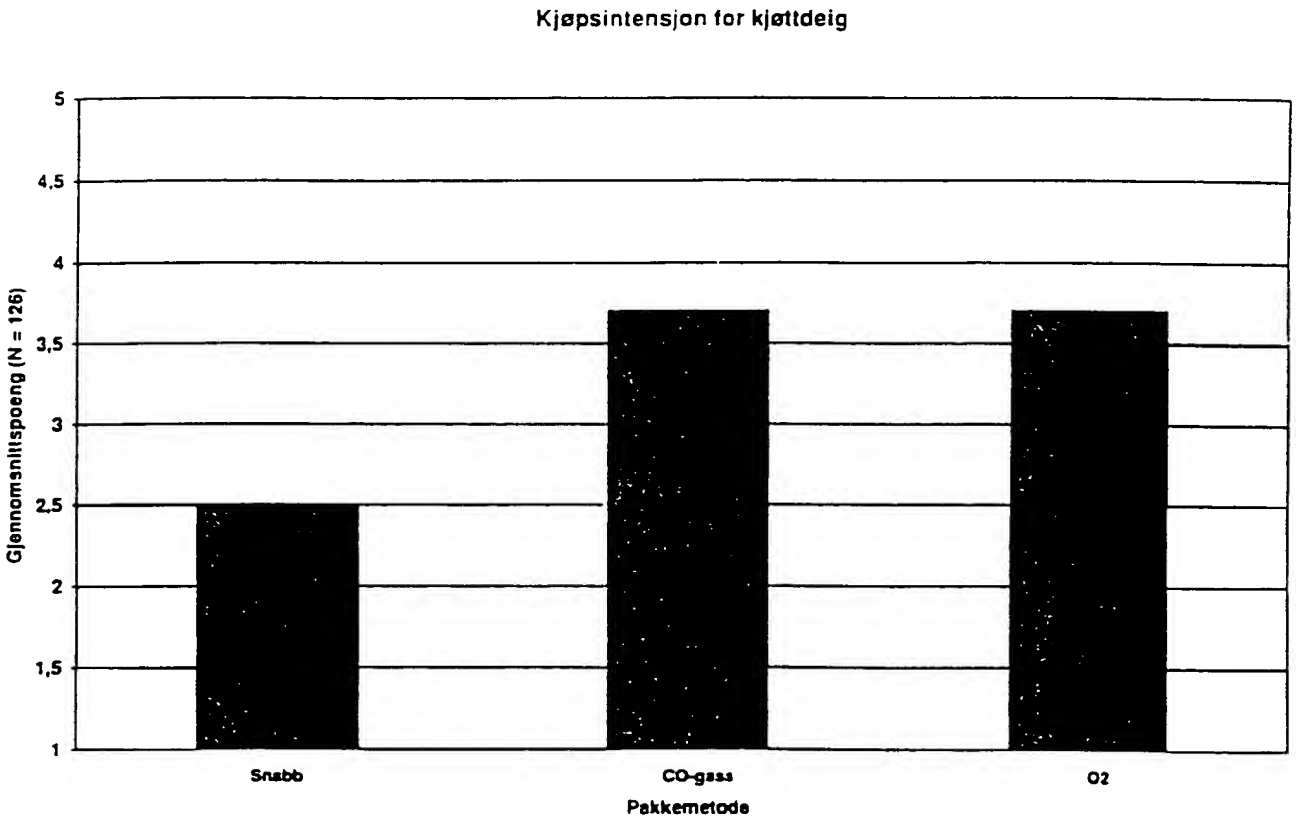
[Beside bar chart] Average score (N=126) [Bar chart]

[Below bar chart] As Sausage CO gas O_2
Packaging Method

Figure 2. *Purchasing tendency for meat products. 1=Will definitely not buy, and 5=Will definitely buy the product as presented in the survey.*

Kjøttdeig
Kjøttdeig pakket som snabb ble dårligst likt av forbrukerne (se Figur 2). Kjøttdeig pakket i CO-gass og kjøttdeig pakket i O_2-atmosfære fikk samme gjennomsnitts-poeng for kjøpsintensjon. Dette resultatet gjaldt uavhengig av forbrukernes alder og kjønn.

Kommentarer fra forbrukere:
Snabbfilm skjuler innholdet.



***Figur 2.** Kjøpsintensjon av kjøttvarer. 1= Vil sikkert ikke kjøpe og 5 = Vil sikkert kjøpe produktet slik det ble presentert i testen*

Pork Chops
Pork chops packaged in CO gas received the highest average score for purchasing tendency. pork chops packaged in O_2 gas received the second highest score and pork chops packaged with oxygen absorber received the lowest average score (see Figure 3). This result occurred regardless of consumer age and gender.

Comments from consumers:
The pork chops packaged with absorber look gray/brown – are they old? expired?

Sample packaged with CO and O_2: nitrite added?

[Above bar chart] **Purchasing Tendency for Ground Meat**

[Beside bar chart] Average score (N=126) [Bar chart]

[Below bar chart] O_2 absorber CO gas O_2
Packaging Method

Figure 3. *Purchasing tendency for meat products. 1=Will definitely not buy. and 5=Will definitely buy the product as presented in the survey.*

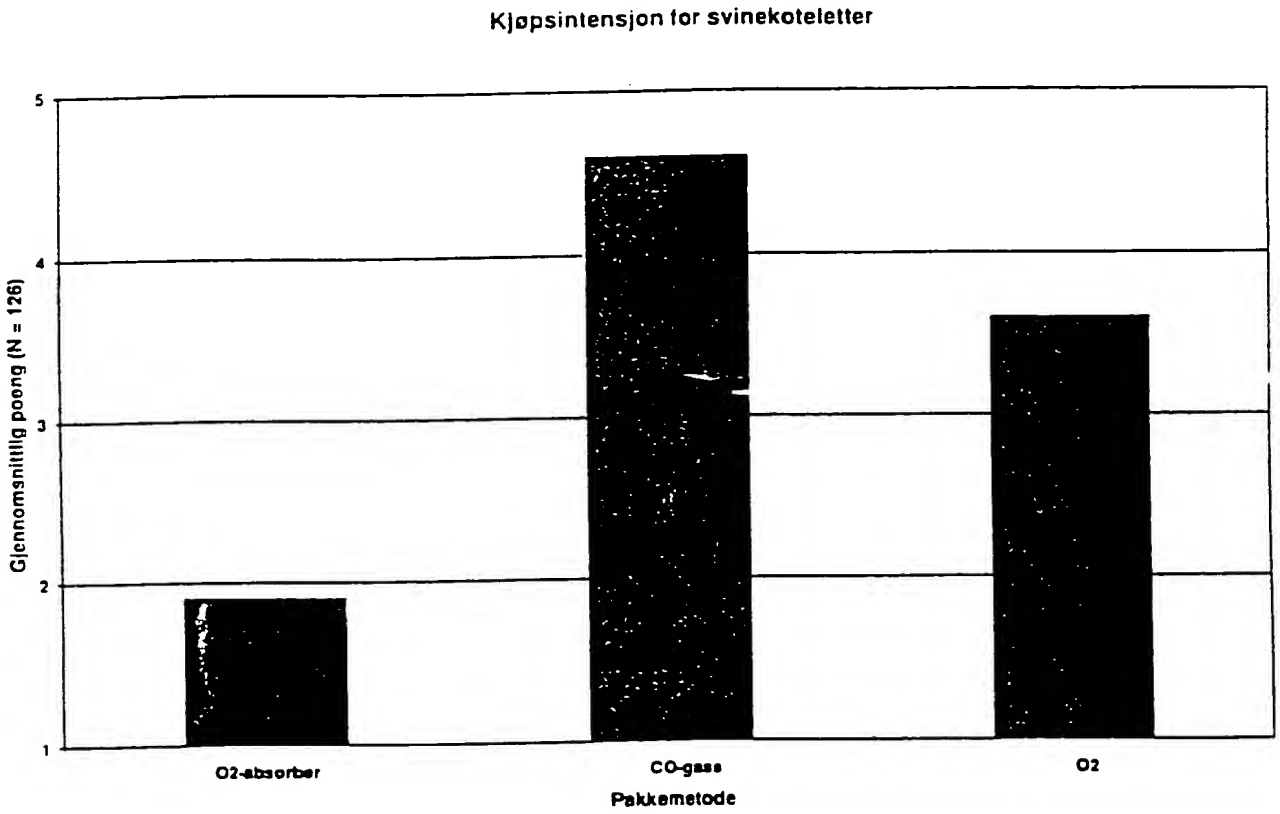
Svinekoteletter

Svinekoteletter pakket i CO-atmosfære fikk høyest gjennomsnittlig poeng for kjøpsintensjon, svinekoteletter pakket i O2-atmosfære fikk nest høyest poeng og svinekoteletter pakket med oksygen absorber fikk lavest gjennomsnittlig poeng (se Figur 3). Dette resultatet gjaldt uavhengig av forbrukernes alder og kjønn.

Kommentarer fra forbrukere:

Koteletter med absorber ser grå/brun ut - er den gammel?, over holdbarhetsdato?

CO- & O_2 -pakket prøve: tilsatt nitritt?



Figur 3. Kjøpsintensjon av kjøttvarer. 1= Vil sikkert ikke kjøpe og 5 = Vil sikkert kjøpe produktet slik det ble presentert i testen

Top Loin
Top loin packaged in CO gas and in O_2 gas received approximately the same average score for purchasing tendency (see Figure 4). Vacuum packaged top loin received a lower score for purchasing tendency than the two aforementioned samples. Men indicated roughly equivalent purchasing tendencies for the three varieties, while women indicated the highest purchasing tendency for top loin packaged in CO gas, followed by top loin packaged in O_2 gas, and the lowest purchasing tendency for vacuum packaged top loin.

Comments from consumers:
Sample packaged in CO and O_2: nitrite added?

Sample packaged in CO: "artificial" sides.

Vacuum packaged sample: looks as if it has been squeezed.

[Above bar chart] **Purchasing Tendency for Top Loin**

[Beside bar chart] Average score (N=125) [Bar chart]

[Below bar chart] Vacuum CO gas O_2
Packaging Method

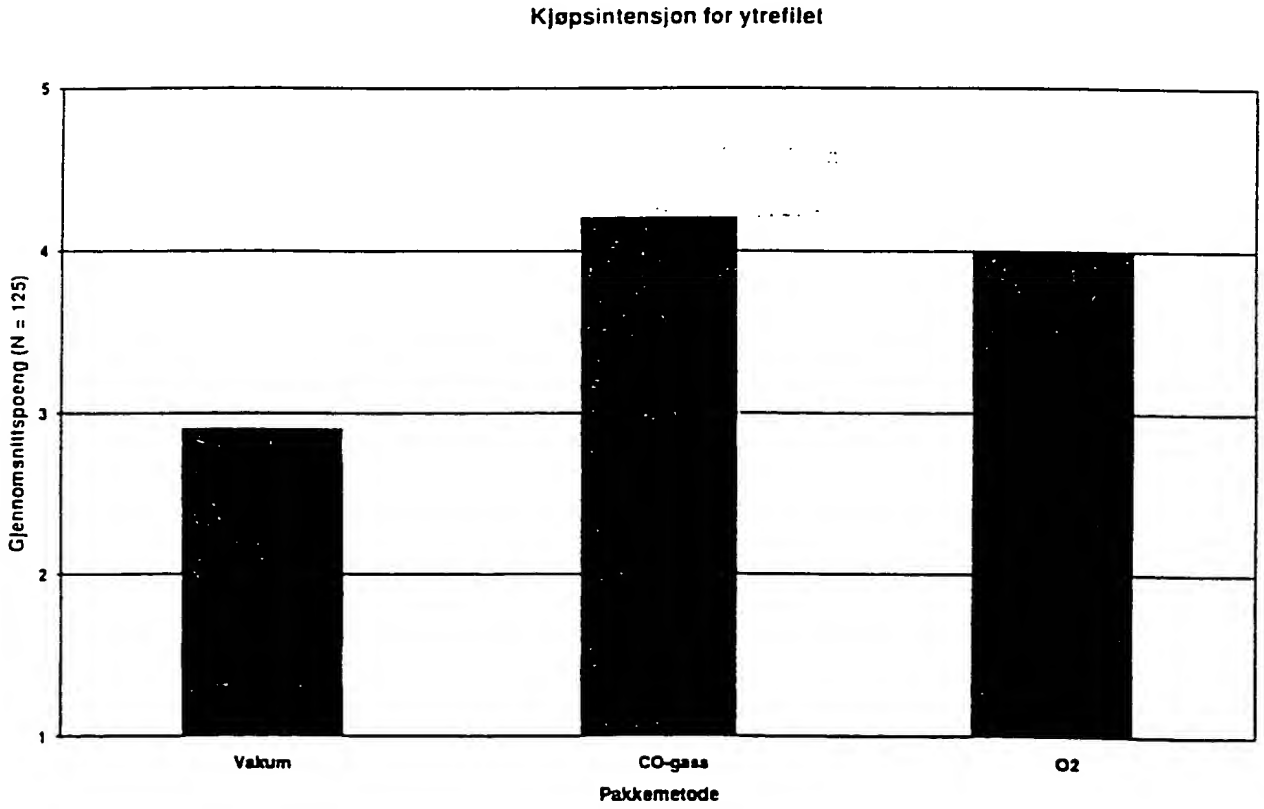
Figure 4. *Purchasing tendency for meat products. 1=Will definitely not buy and 5=Will definitely buy the product as presented in the survey.*

Ytrefilet
Ytrefilet pakket i CO-gass og i O_2-gass fikk omtrent samme gjennomsnittlig poeng for kjøpsintensjon (se Figur 4). Vakuumpakket ytrefilet fikk lavere poeng for kjøpsintensjon enn de to førstnevnte prøvene. Menn anga tilsvarende kjøpsintensjon for de tre variantene, mens kvinner ga høyest kjøpsintensjon for ytrefilet pakket i CO-gass, dernest ytrefilet pakket i O2-atmosfære og lavest kjøpsintensjon for vakuumpakket ytrefilet.

<u>Kommentarer fra forbrukere:</u>
CO- & O_2 -pakket prøve: tilsatt nitritt?

CO-pakket prøve: "kunstig" rand.

Vakuumpakket prøve: ser ut som den er trykka på.



Figur 4. Kjøpsintensjon av kjøttvarer. 1= Vil sikkert ikke kjøpe og 5 = Vil sikkert kjøpe produktet slik det ble presentert i testen.

4. Conclusion

Ground Meat: Ground meat packaged in CO gas and ground meat packaged in O_2 gas received the same average score for purchasing tendency, while ground meat packaged as sausage received the lowest score for purchasing tendency.

Pork Chops: Pork chops packaged in CO gas received the highest score for purchasing tendency, pork chops packaged in O_2 gas received the second highest total score, while pork chops packaged with oxygen absorber received the lowest score.

Top Loin: Top loin packaged in CO gas and in O_2 gas received approximately the same average score for purchasing tendency, and vacuum packaged top loin received the lowest score for purchasing tendency.

Comments
This type of survey does not have representative sampling of consumers in terms of the population as a whole or a specific population segment. The make up of the survey represents a model for a purchasing situation. These circumstances must be taken into account when interpreting the results.

4. Konklusjon

Kjøttdeig: Kjøttdeig pakket i CO-gass og kjøttdeig pakket i O_2-atmosfære fikk samme gjennomsnitt poeng for kjøpsintensjon, mens kjøttdeig pakket som snabb fikk lavest poeng for kjøpsintensjon.

Svinekoteletter: Svinekoteletter pakket i CO-atmosfære fikk høyest poeng for kjøpsintensjon, svinekoteletter pakket i O2-atmosfære fikk nest høyest poeng og svinekoteletter pakket med oksygen absorber fikk lavest poeng.

Ytrefilet: Ytrefilet pakket i CO-gass og i O_2-gass fikk omtrent samme gjennomsnittlig poeng for kjøpsintensjon, og vakuumpakket ytrefilet fikk lavest poeng for kjøps-intensjon.

Kommentarer

Denne typen test har ikke et representativt utvalg forbrukere i forhold til befolkningen generelt eller en bestemt gruppe i befolkningen. Opplegget i testen er en modell for en kjøpssituasjon. Disse forholdene må tas i betraktning ved tolkning av resultatene.

ATTACHMENT 1

Overview of Results from Consumer Study of Meat Products

	Average	*Standard Deviation*	*Median*
Ground Meat (N=126)			
As sausage	2.5	1.5	2
CO gas	3.7	1.4	4
O_2	3.7	1.4	4
Pork Chops (N=126)			
O_2 absorber	1.9	1.3	1
CO gas	4.6	0.7	5
O_2	3.6	1.4	4
Top Loin (N=125)			
Vacuum	2.9	1.6	3
CO gas	4.2	1.1	4.5
O_2	4.0	1.1	4

VEDLEGG 1

Oversikt over resultater fra forbrukertest av kjøttvarer

	Gjennomsnitt	*Standardavvik*	*Median*
Kjøttdeig (N = 126)			
Snabb	2.5	1.5	2
CO-gass	3.7	1.4	4
O_2	3.7	1.4	4
Svinekoteletter (N = 126)			
O_2-absorber	1.9	1.3	1
CO-gass	4.6	0.7	5
O_2	3.6	1.4	4
Ytrefilet (N = 125)			
Vakuum	2.9	1.6	3
CO-gass	4.2	1.1	4.5
O_2	4.0	1.1	4

Prosjektmedarbeidere:

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Ansvarlig for *prøvemottak og lyssetting*:	Oddvin Sørheim
Ansvarlig for *praktisk gjennomføring*:	Inger Johanne Fjøsne
Øvrige deltakere i gjennomføring:	Asgeir Nilsen Janne Haugdahl Vibeke Høst Oddvin Sørheim
Ansvarlig for *statistisk bearbeiding*:	Per Lea

(4)

English summary

DISCOLORATION OF MEAT AS AN INDICATOR OF LEAKAGES IN PACKAGES CONTAINING A CO GAS MIXTURE

Oddvin Sørheim, MATFORSK, Norwegian Food Research Institute, Oslovn. 1, 1430 Ås, Norway

The aim of the experiment was to study discoloration of meat packaged in a gas mixture of 60 % CO_2/40 % N_2/ 0.4 % CO with different concentrations of residual O_2 added. Tests were performed on ground beef with 1 % NaCl, aged beef loin steaks and pork chops. Leakages were simulated by injecting different amounts of air with a syringe into the packages after two days storage. Discoloration of the meat was measured as reduction in a^* (redness) values and evaluated visually. Ground beef had a low tolerance level of residual O_2 because it was discoloured in atmospheres containing more than 1 % O_2. Beef loin steaks and pork chops were slightly discoloured in more than 2 and 5 % O_2, respectively. The results suggest that discoloration can be an indicator of leakages for ground beef, but not for beef loin steaks and pork chops.

COMMISSIONED REPORT

MATFORSK – Norwegian Food Research Institute

Osloveien 1, N-1430 Ås
Tel: (+47) 64 97 01 00

Report No.: O-7224.col
Availability: Confidential

Report Title: Meat Discoloration as an Indicator of Leaks in Packaging with CO Gas Mixtures	**Date:** November 28, 1996
Project Manager/Author: Oddvin Sørheim	**Signature of Project Manager:** [Signature]
Head of Department: Astrid Nilsson	**Signature of Head of Department:** [Signature]
Department: Product and Raw Material Science	**Project No:** O-7224.col
Commissioned by: Norsk Kjøtt [Norwegian Meat]	**Commissioner's contact:** Truls Nesbakken

Summary/Abstract:

Tests were carried out to find the tolerance limits for residual O_2 for discoloration of meat packaged in CO gas mixture with simulated leak. Various concentrations of air were added to the packages of ground meat, top loin and pork chops with a mixture of 60% CO_2 / 40% N_2 / 0.4% CO two days after packaging. Ground meat packaged in gas containing more than 1% O_2 was clearly discolored, while top loin and pork chops, respectively packaged in gas containing more than 2 and 5% O_2 showed only minor discoloration. The results indicate that discoloration can serve as an indicator of leakage for ground meat, but not for top loin and pork chops.

OPPDRAGSRAPPORT

MATFORSK - Norsk institutt for næringsmiddelforskning

Osloveien 1, 1430 Ås
Tlf. 64 97 01 00

Rapportnummer:

O-7224.col

Tilgjengelighet:
Fortruleg

Rapportens tittel: Misfarging av kjøt som indikator på lekkasje i pakningar med CO-gassblanding	**Dato:** 28.11.96
Prosjektleder/forfatter: Oddvin Sørheim	**Prosjektleders signatur:**
Avdelingsleder: Astrid Nilsson	**Avdelingsleders signatur:**
Avdeling: Produkt- og råvarekunnskap	**Prosjektnummer:** O-7224.col
Oppdragsgiver: Norsk Kjøtt	**Oppdragsgivers ref:** Truls Nesbakken

Sammendrag/ekstrakt:

Forsøk vart gjennomført for å finna toleransegrenser for rest-O_2 for misfarging av kjøt pakka i CO-gassblanding med simulert lekkasje. Pakningar av kjøtdeig, ytrefilet og svinekoteletar med 60 % CO_2/ 40 % N_2/ 0,4 % CO vart tilsett ulike konsentrasjonar luft 2 dagar etter pakking. Kjøtdeig vart tydeleg misfarga i atmosfærer over 1 % O_2, medan ytrefilet og svinekotelettar berre var svakt misfarga med over hhv 2 og 5 % O_2 i atmosfæra. Resultata tyder på at misfarging kan fungera som ein indikator på lekkasje for kjøtdeig, men ikkje for ytrefilet og svinekotelettar.

MATFORSK – Norwegian Food Research Institute

Meat Discoloration as an Indicator of Leakage in Packages with CO Gas Mixtures

Purpose

The purpose of the survey was to find the tolerance limits for residual O_2 with regard to discoloration of ground meat, top loin and pork chops packaged in a CO gas mixture.

Implementation of the Study

Samples of ground meat with 1% NaCl (20 pieces), tenderized top loin of beef (18 pieces) and pork chops (14 pieces) were gas packed on a Ilapak Delta 2000 machine (Ilapak, Switzerland) on a tray in BDF 550 shrink film (Cryovac). The gas mixture consisted of 60% CO_2 / 40% N_2 / 0.4% CO. The samples were stored out of light at 4°C. After two days of storage, air was added to the packages to increase the O_2 content, i.e. a simulated leak. This was done by sucking out the gas in the package and replacing it with air by means of a syringe and a septa . 0-2.0% O_2 was added to the ground meat, 0-3.2% O_2 was added to the top loin, and 0-13.9% O_2 was added to the pork chops, in all cases with a spectrum of O_2 concentration in their respective ranges. After the replacement of gases, the concentrations of O2 and CO_2 were measured by means of two Toray instruments, type LC 700F and PG-100 (Toray Eng., Japan). The remaining storage time before unwrapping was 2 days for ground meat and 5 days for both top loin and pork chops.

Upon unwrapping, the O_2 and CO_2 concentrations in the packages were once again measured. Two judges then visually judged the color of the unopened packages according to a scale (1=fresh meat red, 2=dark red, 3=somewhat discolored, 4=moderately discolored, 5=extremely discolored). The packages were then opened, and the color was measured with a Minolta Chroma Meter CR-300 (Minolta Camera Co., Japan) directly on the surface of the meat within 1 minute of opening. The instrument had light source D_{65} at 8 mm aperture, and the color was measured in CIE (1976) L* (luminosity), a* (redness) and b* (yellowness). Lastly, the pH was measured directly in the meat with a Ingold Xerolyt electrode (Mettler-Toledo A.G., Switzerland).

Results and Discussion

The correlation between discoloration upon unwrapping and O_2 concentration when replacing the gas proved to best be expressed by an a* value (redness) and visual color evaluation. Attached are a plot of the a* and O_2 concentration for ground meat, top loin and pork chops; see figures 1, 2, and 3. The correlation coefficients for the three products were calculated to -0.71, -0.33, and -0.51. The relatively low coefficients are partly due to the large spread of the measured values and partly because the correlation between a* and O_2 does not appear to be linear.

For ground meat we found a reduction of approximately 4-5 a* values from 0 to 1% O_2. A reduction of a* to this degree is readily apparent. Samples stored in 1% or higher levels of O_2 had a score of between 3 and 4 on the color scale, i.e. slight to moderate discoloration. The results indicate that the tolerance limit for discoloration of ground meat in CO mixture is approximately 1% O_2.

Misfarging av kjøt som indikator på lekkasje i pakningar med CO-gassblanding

Formål

Hensikten med forsøket var å finna toleransegrenser for rest-O_2 mht misfarging av kjøtdeig, ytrefilet og svinekotelettar pakka i CO-gassblanding.

Gjennomføring av forsøket

Prøver av kjøtdeig m/1% NaCl (20 stk), mørna ytrefilet av storfe (18 stk) og svinekotelettar (14 stk) vart gasspakka på ei Ilapak Delta 2000 maskin (Ilapak, Sveits) på skål i BDF 550 krympefilm (Cryovac). Gassblandinga bestod av 60 % CO_2/ 40 % N_2/ 0,4 % CO. Prøvene vart lagra mørkt ved 4 °C. Etter 2 dagar lagring vart pakningane tilførte luft for å auka innhaldet av O_2, dvs ein simulert lekkasje. Dette vart gjort ved å trekka ut pakkegassen og erstatta den med luft gjennom eit septa vha ei sprøyte. Kjøtdeig vart tilsett 0-2,0 % O_2, ytrefilet 0-3,2 % O_2 og svinekotelettar 0-13,9 % O_2, alle med eit spekter av O_2-konsentrasjonar i sine område. Etter utskiftinga av atmosfærer vart O_2- og CO_2-konsentrasjonane målte med to Toray-instrument, type LC 700F og PG-100 (Toray Eng., Japan). Den vidare lagringstida før uttak var 2 dagar for kjøtdeig, og 5 dagar for både ytrefilet og svinekotelettar.

Ved uttak vart pakningane på ny målte for O_2- og CO_2-konsentrasjonar. Kjøtet vart så bedømt visuelt av to dommarar for farge i uopna pakning etter ein skala (1 = frisk raud, 2 = mørk raud, 3 = svakt misfarga, 4 = moderat misfarga, 5 = ekstremt misfarga). Deretter vart pakningane opna, og farge vart målt med eit Minolta Chroma Meter CR-300 (Minolta Camera Co., Japan) direkte på kjøtoverflata innan 1 minutt etter opning. Instrumentet hadde lyskjelde D_{65} med 8 mm lysopning, og fargen vart uttrykt i CIE (1976) L^* (lyshet), a^* (raudhet) og b^* (gulhet). Til sist vart pH målt direkte i kjøtet med ein Ingold Xerolyt elektrode (Mettler-Toledo A.G., Sveits).

Resultat og diskusjon

Samanhengen mellom misfarging ved uttak og O_2-konsentrasjon ved utskifting av atmosfæra viste seg å vera best uttrykt gjennom a^*-verdi (raudhet) og visuell fargebedømming. Vedlagt følgjer plot for a^* og O_2-konsentrasjon for kjøtdeig, ytrefilet og svinekotelettar; sjå figur 1, 2 og 3. Korrelasjonskoeffesientane vart berekna til -0,71, -0,33 og -0,51 for dei tre produkta. Dei relativt låge koeffesientane skuldast dels stor spredning i måleverdiane og dels at samanhengen mellom a^* og O_2 ikkje synest vera lineær.

For kjøtdeig fann vi ein reduksjon på ca. 4-5 a^*-verdiar frå 0 til 1 % O_2. Ein nedgang i a^* av denne storleiken er tydeleg synleg. Prøver lagra i 1 % eller høgare O_2 hadde poeng mellom 3 og 4 på fargeskalaen, dvs svakt til moderat misfarga. Resultata tyder på at toleransegrensa for misfarging av kjøtdeig i CO-blandinga er på ca 1 % O_2.

For top loin, on the other hand, a smaller decrease in a* and a weak correlation between a* and O_2 concentration were found. However, there seemed to be a reduction of about 2 a* values between 0 and 2% O_2, with a color scale score of about 3 on samples stored in over 2% O_2. This indicates a weak discoloration with a tolerance limit of approximately 2 % O_2 for top loin.

The color of pork chops proved to be only slightly affected by the O_2 concentration in the packaging gas, even when up to 2/3 of the gas was replaced with air. We found a reduction of 1 to 1.5 a* values between 0 and 5% O_2 in the package gas, but this barely registered as discoloration with a score of 2-3 on the color scale.

The pH values at the end of the leak test were on average 5.59, 5.62 and 5.42 for ground meat, top loin and pork chops respectively.

Between the start and the end of the leak tests, we measured a reduction in the O_2 concentrations of 80, 40 and 30 % for ground meat, top loin and pork chops respectively. This reduction can be due to meat respiration or consumption of O_2 by bacteria. Ground meat has a high consumption of O_2 due to a large surface area exposed to surrounding gas and frequently higher bacteria counts than whole meat.

The significance of residual O_2 in package gas with regard to discoloration and microbiological storage life has been discussed previously in the report "Fresh Meat in Consumer Packaging - an Evaluation of Various Packaging Methods and Their Effect on Meat Quality." For storage in gas containing CO_2 and/or N_2 without the presence of CO, tolerance limits for discoloration have been found to be below 0.1 and 0.5% O_2 for beef and pork respectively. Tests on pork has shown that the microbiological storage life was reduced when the package gas contained more than 2-4% O_2.

The ground meat containing 1% sodium that was tested in this survey, had obvious discoloration when the CO mixture contained at least 1% O_2. Sodium functions as a pro-oxidant, and will usually intensify or accelerate the discoloration of the meat. It is therefore likely that consumers will react on the color of ground meat when small leaks in the packaging exist. For top loin and pork chops, however, there is little likelihood that the minor discoloration occurring at above 2 and 5% O_2 will serve as an indicator of leakage to the regular consumer. The lighting in store refrigerating counters will often conceal minor color nuances. All in all, these results show that CO has a strong bond to the myoglobine in whole, unsalted meat, which prevents the carbon myoglobine from being destabilized by O_2 in the gas. Hence, discoloration is not a good indicator with regard to alerting consumers of leaks and risk of increased bacterial growth in meat such as top loin and pork chops.

Thanks
We are grateful to Frank Lundby for his valuable technical assistance.

For ytrefilet, derimot, vart det funne ein mindre nedgang i a* og ein svak samanheng mellom a* og O_2-konsentrasjon. Det syntest likevel å vera ein nedgang på ca 2 a*-verdiar mellom 0 og 2 % O_2, med poeng på fargeskalaen omkring 3 på prøver lagra i over 2 % O_2. Dette indikerer ei svak misfarging med ei toleransegrense på omlag 2 % O_2 for ytrefilet.

Fargen på svinekotelettar viste seg å svært lite påverka av O_2-konsentrasjonen i pakke-atmosfæra, sjølv med utskifting av opp til 2/3 av atmosfæra med luft. Vi fann ein nedgang på 1-1,5 a*-verdiar frå 0 til 5 % O_2 i atmosfæra, men dette kunne knapt registrerast som misfarging med poeng på 2-3 på fargeskalaen.

pH ved avslutning av lekkasjetesten var i gjennomsnitt 5,59, 5,62 og 5,42 for hhv kjøtdeig, ytrefilet og svinekotelettar.

Mellom start og avslutning av lekkasjetestane målte vi ein nedgang i O_2-konsentrasjonar på ca 80, 40 og 30 % for hhv kjøtdeig, ytrefilet og svinekotelettar. Denne nedgangen kan skuldast både respirasjon i kjøtet og forbruk av O_2 av bakteriar. Kjøtdeig har eit høgt forbruk av O_2 pga stor overflate mot atmosfæra og gjerne høgare bakterietal enn heilt kjøt.

Betydningen av rest-O_2 i pakke-atmosfærer for misfarging og mikrobiolgisk holdbarhet er tidlegare drøfta i rapporten "Ferskt kjøt i forbrukarpakning - ei vurdering av ulike pakkemetodar og deira verknad på kjøtkvalitet". For lagring i atmosfærer med CO_2 og/eller N_2 utan CO til stades er det funne toleransegrenser for misfarging på under 0,1 og 0,5 % O_2 for hhv storfe- og svinekjøt. Forsøk med svinekjøt har vist at den mikrobiologiske holdbarhetstida vart forkorta når atmosfæra inneheldt meir enn 2-4 % O_2.

Kjøtdeigen med 1 % salt som vart testa i dette forsøket, var tydeleg misfarga med 1 % eller meir O_2 i CO-blandinga. Salt verkar som ein pro-oksidant og vil som regel forsterka eller framskunda misfarging av kjøt. Det er derfor sannsynleg at forbrukaren vil reagera på fargen på kjøtdeig med små lekkasjar i pakningen. For ytrefilet og svinekotelettar er det derimot lite truleg at den svake misfarginga med over 2 og 5 % O_2 vil fungera som ein indikator på lekkasje for ein vanleg forbrukar. Lyssetjinga i butikkane sine kjølediskar vil ofte kamuflera små fargenyansar. Samla viser desse resultata at CO har ei sterk binding til myoglobinet i heilt, usalta kjøt, som fører til at karboksymyoglobinet vanskeleg let seg destabilisera av O_2 i atmosfæra. Misfarging vil derfor ikkje vera nokon god indikator for å åtvara forbrukaren mot lekkasjar og risiko for auka bakterievekst i kjøt som ytrefilet og svinekotelettar.

Takk
Frank Lundby blir takka god teknisk assistanse.

[Left-hand side of graph] a* [Plot]

[Below graph] % Oxygen

Figure 1 *The correlation between a* (redness) and O_2 concentration for ground meat packaged in a mixture of 60% CO_2 / 40% N_2 /0.4% CO after two days storage at* 4°C. n=20, r=-0.71.

[Left-hand side of graph] a* [Plot]

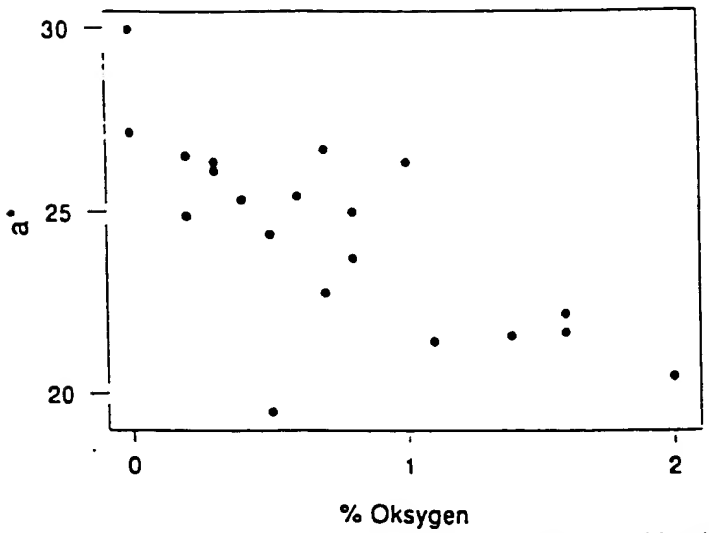
[Below graph] % Oxygen

Figure 2 *The correlation between a* (redness) and O_2 concentration for top loin packaged in a mixture of 60% CO_2 / 40% N_2 /0.4% CO after five days storage at* 4°C. n=18, r=-0.33.

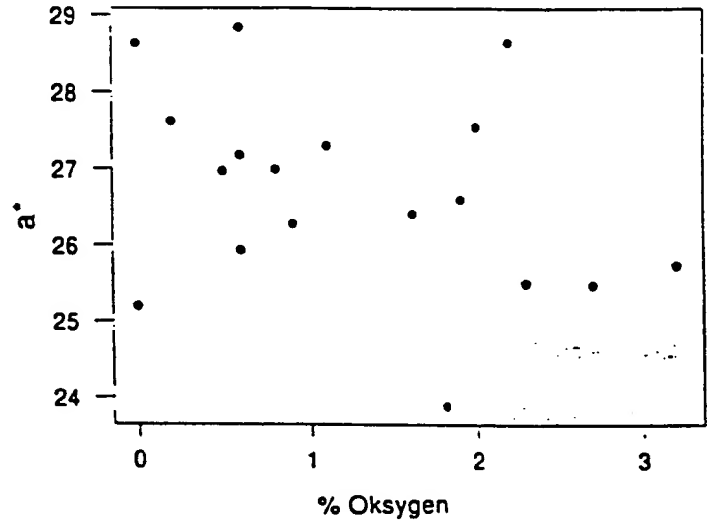
[Left-hand side of graph] a* [Plot]

[Below graph] % Oxygen

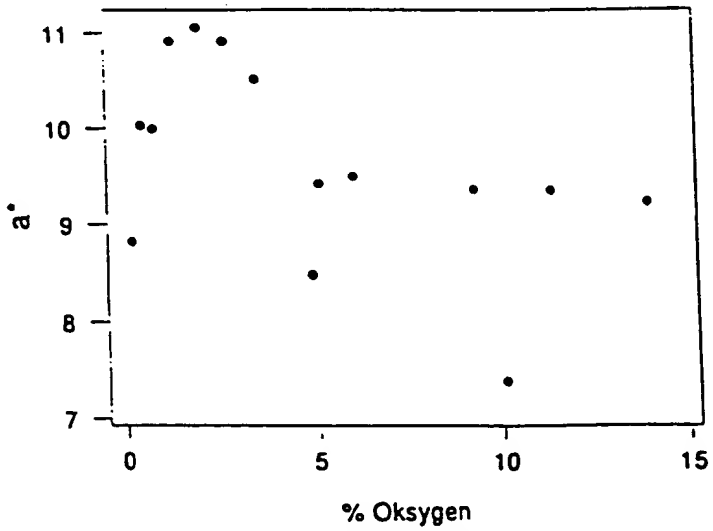
Figure 3 *The correlation between a* (redness) and O_2 concentration for pork chops packaged in a mixture of 60% CO_2 / 40% N_2 /0.4% CO after five days storage at* 4°C. n=14, r=-0.51.



Figur 1 Forhold mellom a (raudhet) og O_2-konsentrasjon for kjøtdeig pakka i 60 % CO_2/ 40 % N_2 / 0,4 % CO etter 2 dagar lagring ved 4 °C. n = 20, r = -0,71.*



Figur 2 Forhold mellom a (raudhet) og O_2-konsentrasjon for ytrefilet pakka i 60 % CO_2/ 40 % N_2/ 0,4 % CO etter 5 dagar lagring ved 4 °C. n = 18, r = -0,33.*



Figur 3 Forhold mellom a (raudhet) og O_2-konsentrasjon for svinekotelettar pakka i 60 % CO_2/ 40 % N_2/ 0,4 % CO lagra i 5 dagar ved 4 °C. n = 14, r = -0,51.*

(5)

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Technological, hygienic and toxicological aspects of carbon monoxide used in modified-atmosphere packaging of meat

Oddvin Sørheim, Tore Aune and Truls Nesbakken

Retail meat can be packaged in gas mixtures containing 60–70% carbon dioxide (CO_2), 30–40% nitrogen (N_2) and <0.5% carbon monoxide (CO). This gas mixture with CO provides a unique combination of a long microbiological shelf life and a stable, cherry red colour of the meat. The shelf life of meat packaged in the CO mixture is longer than that of meat packaged in the commonly used atmospheres with high oxygen (O_2), that is, approximately 70% O_2 and 30% CO_2. The consumption of meat that has been packaged in a CO mixture will result in only negligible levels of carboxyhaemoglobin in the blood. It is highly improbable that the use of CO in the packaging of meat will present a toxic threat to consumers.

Modified-atmosphere packaging (MAP) is gaining increasing application in modern food distribution. Meat intended for retail sale can either be wrapped in vapour-tight, oxygen-permeable films or packaged in gas-tight films with a modified atmosphere (MA). The main purposes of the MAP of meat are twofold: to ensure the microbiological shelf life and the attractive red colour of the product. Consumers frequently interpret the colour of meat on retail display as an indicator of wholesomeness[1].

CO is a colourless, odourless and tasteless gas. It is produced mainly through incomplete combustion of carbon-containing materials. Natural background levels of CO are 0.01–0.9 mg/m^3 (Ref. 2). In urban areas, 8-h mean concentrations of CO (i.e. mean CO concentrations are measured for each possible 8-h interval during a 24-h period, then averaged) are generally <20 mg/m^3; however, maximum 8-h concentrations (i.e. the maximum mean concentration found during any one 8-h period) of up to 60 mg/m^3 have been recorded[2]. By far the most common cause of elevated CO concentrations in the blood is tobacco smoking[3].

A challenge in the MAP of retail meat is the stabilization of the red colour of the product. The positive effect of CO on meat colour was known and patented over 100 years ago[4]. Despite this knowledge, CO has to date been applied commercially only to a limited extent in the MAP of meat. During the past 10 years, the Norwegian meat industry has been using a gas mixture of 60–70% CO_2, 30–40% N_2 and 0.3–0.4% CO for the packaging of fresh retail meat, namely beef, pork and lamb. This gas mixture with CO maintains a stable, cherry red colour combined with a long microbiological shelf life of the meat. The market share of retail meat packaged in this CO mixture in Norway is estimated at 50–60% (Dag Hallan, pers. commun.). In addition, some meat is also initially bulk-packaged in the CO mixture, and thereafter repackaged on trays with O_2-permeable films in retail outlets. In other European countries not using such CO mixtures, market shares of retail meat packaged in atmospheres with a high O_2 concentration, with considerably shorter shelf lifes, have been reported to be only 10–40%[5,6].

In this article, we have evaluated the toxicological aspects of CO, and its mode of action and application in the MAP of meat.

Technological and hygienic aspects of CO as a packaging gas for meat

Gases for MAP

The most commonly used gases for the MAP of meat are CO_2, N_2 and O_2, although other gases, including CO, nitrous oxide, argon and ozone, have been tried to a limited extent[4]. CO_2 inhibits the growth of many microorganisms, but it has no effect *per se* on the colour of meat[6]. CO_2 is absorbed in meat and fat tissue at a ratio of ~1 litre of gas per kg of tissue[7]. N_2 affects neither the microbiology nor the colour of the meat, but prevents packages from collapsing, because it is not absorbed by the product. O_2 supports the growth of aerobic microorganisms; thus, removal of O_2 from the MA will extend the microbiological shelf life. High O_2 concentrations cause meat to have a temporary bright red colour; oxygen binds to the muscle pigment myoglobin, forming oxymyoglobin, which is gradually oxidized to grey–green–brown metmyoglobin[8] (Fig. 1). Gases for the packaging of meat are seldom used alone, but in mixtures, which vary according to the application. Examples of different gas mixtures for the MAP of meat are discussed below.

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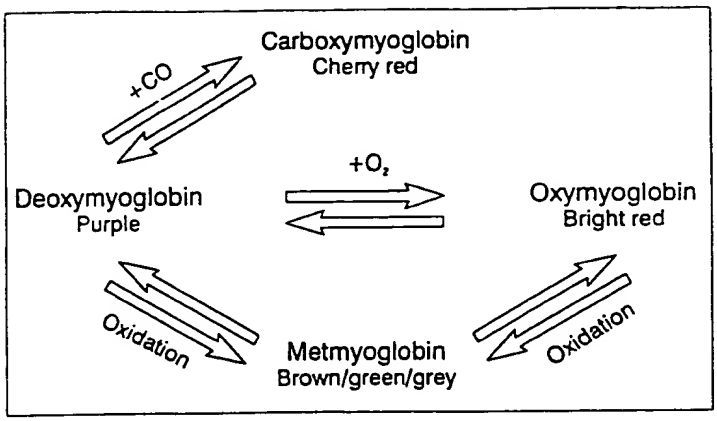

Fig. 1
Myoglobin forms and colour of meat.

CO and colour

The main function of low levels of CO in MAs is to give meat a stable, cherry red colour, as a result of strong binding of CO to myoglobin and the formation of carboxymyoglobin[9] (Fig. 1). Although a substantial increase in the shelf life of meat can be obtained by using various MAs, it is often limited by discolouration due to the oxidation of myoglobin to metmyoglobin. This discolouration can be prevented by the inclusion of a low level of CO in the gas mixture.

Carboxymyoglobin is more resistant to oxidation than oxymyoglobin, owing to the stronger binding of CO to the iron-porphyrin site on the myoglobin molecule[10]. CO at concentrations of 1–5% increased the reduction of metmyoglobin, even in the presence of air[11].

Examples of different gas mixtures that contain CO for the packaging of meat are given in Table 1. A mixture of 2% CO and 98% air was very effective in stabilizing the colour of beef for 15 d, compared with 5 d in air alone[12]. Ground beef patties stored in an atmosphere of 1% CO/50% CO_2/49% air retained a stable, red colour for at least 6 d, whereas the colour of samples stored in air was stable for only 3 d[13].

The colour of beef was analysed during storage in MAs containing N_2 with 0.5–10% CO. Levels of CO >0.5% resulted in a stable, red colour for >30 d, whereas discolouration occurred after 5 d storage in control samples packaged in air[14]. In addition, samples of this beef were exposed to pure CO for 2–16 h before packaging in air. The colour stability of the CO-treated samples was no greater than that of untreated samples. However, in other experiments the exposure of beef to CO before vacuum packaging increased its redness and colour acceptability during subsequent chilled or frozen storage[9,17]. Beef loin roasts stored in 1% CO/51% CO_2/30% O_2/18% N_2 were shown to have lower levels of metmyoglobin on their surface than vacuum-packaged roasts. After a further 4 d on retail display, steaks from the roasts underwent less discolouration if they had previously been stored in the CO mixture[15]. Ground beef and beef loin steaks packaged in 1% CO/50% CO_2/25% N_2/24% O_2 or 1% CO/20% CO_2/9% N_2/70% O_2 retained a stable colour for 29 d[16]. Similarly, beef loin steaks packaged in 0.4% CO/60% CO_2/40% N_2 maintained a stable, cherry red colour for up to 22 d[18]. Experiments with beef and higher levels of CO, that is, 2% CO/20% CO_2/78% N_2, resulted in meat that had a stable colour; however, its colour was characterized as 'too artificial' by a sensory panel[6].

Based on the cited literature, the presence of 0.4–1.0% CO in MAs used for the packaging of meat seems sufficient to produce a stable, cherry red colour.

Cooked, cured meat products can also benefit from storage in MAs containing CO. Packaging in 1% CO/99% N_2 stabilized the colour of sliced bologna, indicating binding between CO and denatured myoglobin[19].

Under certain circumstances, an undesirable pink or red colour can arise in cooked white meat, such as poultry, and cooked meat products without added nitrite[20]. Such colour problems can sometimes be linked with exposure to CO, which results in similar colours occurring after the use of MAs with CO. For example, roasted turkey was noted to be pink; this was probably due to the presence of CO and nitric oxide in the combustion gases in the oven. The pink colour did not occur when the turkeys were roasted in complete isolation from the oven gases[21]. Combustion engines produce various gases, including CO, which can affect live poultry during transportation to the abattoir. Meat from chickens that were exposed to exhaust fumes immediately before slaughter developed an undesired red colour on cooking[22].

CO and microbiology

Generally, the purpose of most of the experiments investigating the use of CO as a small component of MAs for meat has been to study its effect on colour stability, and more seldom its microbiological aspects. The growth of psychrotropic bacteria on beef stored in MAs containing 0.5–10% CO in N_2 was lower, relative to controls, resulting in an increase in odour shelf life at

Table 1. Applications of carbon monoxide (CO) in the modified-atmosphere packaging of meat

Gas combinations (%)					
CO	CO_2	N_2	O_2	Air	Refs
2				98	12
1	50			49	13
0.5–10		90–99.5			14
1	51	18	30		15
1	50	25	24		16
1	20	9	70		16
2	20	78			6
1–5				95–99	10
100[a]					9, 14, 17
0.4	60	40			18
0.3–0.4	60–70	30–40			[b]

[a] Exposure before packaging
[b] Data supplied by Norwegian meat plants

temperatures in the range of 0–10°C[14]. For example, beef packaged in a MA of 1% CO/99% N_2 had an odour shelf life of 24 d, compared with 18 d in 100% N_2, and 7 d in air at 5°C. However, in another experiment with a MA of 20% CO_2/70% O_2/9% N_2, the addition of 1% CO had no effect on the microbiological growth on ground beef and beef steaks[16]. The presence of bacteriostatic CO_2 in the latter experiment apparently reduced the importance of the effect of CO on the shelf life of the meat. The odour shelf life of steaks of beef loins stored in 0.4% CO/60% CO_2/40% N_2 was 4 d longer than that of steaks stored in 70% O_2/30% CO_2 at 4°C[18]. Beef steaks that were exposed to pure CO before vacuum packaging had an extended shelf life compared with untreated controls. The total aerobic plate, lactic acid bacteria and psychrotropic counts of CO-treated steaks were 1–2 log cycles lower than those of controls after 8 weeks storage at 4°C[17]. In a study using pure bacterial cultures, the presence of CO at a concentration of 5–30% in air had no effect on the growth of *Pseudomonas aeruginosa*, inhibited the growth rate of *Escherichia coli* (in proportion to the concentration of CO), increased the lag phase of *Achromobacter* and inhibited the growth rate of *Pseudomonas fluorescens*[23].

Table 2. Estimate of carboxyhaemoglobin percent (COHb%) in human blood at different concentrations of carbon monoxide (CO) in the atmosphere, depending on the level of physical activity[a]

Exposure		COHb%		
CO concentration (mg/m³)	Time (h)	At rest	Moderate activity	Heavy work
10	8	1.3	1.4	1.4
25	1	1.0	1.5	2.0
40	1	1.3	2.2	2.9

[a]Data taken from Ref. 24

Toxicological aspects of CO

Health effects of CO

CO binds to the iron atom of haemoglobin in red blood cells, forming carboxyhaemoglobin (COHb). The affinity of haemoglobin for CO is ~240 times higher than its affinity for O_2. CO also binds to myoglobin, cytochromes and some enzymes, but these reactions are considered to be of less importance than the formation of COHb[2]. The binding of CO to haemoglobin is reversible, with a half-life of ~4.5 h in individuals who are at rest.

Although CO acts primarily by interfering with O_2 transport, it also reduces the delivery of O_2 to the various tissues[3]. In humans, health effects are mainly manifested in the cardiovascular system, the nervous system and in the foetus.

The COHb concentration in blood, often referred to as the COHb percent (COHb%), is a function of the CO concentration in the air, the exposure time, and the level of physical activity of the individual[24] (see Table 2). At a COHb concentration of ~2.5%, the most sensitive individuals (patients suffering from cardiovascular diseases) display changes in cardiac function and report chest pain. At somewhat higher COHb concentrations, they experience reduced working capacity and the onset of angina pectoris on exercise[25,26]. In healthy adults, no adverse health effects were described at CO concentrations that result in <5% COHb[27].

A small amount of CO is formed naturally in the human body, owing to the breakdown of haemoproteins.

Table 3. Association between different carboxyhaemoglobin (COHb) levels in blood and health effects[a]

COHb%	Observed health effects
≥50	Unconsciousness, lethal if not treated
≥30	Headache, nausea, vomiting, dizziness
≥10	Life threatening for heart and lung patients; headache in other individuals
≥5	Reduced maximum oxygen consumption during exercise in healthy individuals
≥5	Reduced visual perception, learning ability and fine motor performance
≥5	The foetus can be affected on carbon monoxide exposure of pregnant women
≥2.9	Angina patients endure less physical strain before experiencing attack
≥2.3	Reduced physical working capacity, especially endurance
≥2	Possible reduction in attention and ability to concentrate
≥2	Signs of local lack of oxygen and onset of chest pain in heart patients

[a]Data taken from Refs 25–27

Such production leads to a COHb concentration of ~0.5%. The average COHb concentration in non-smokers is 1.2–1.5%, and ~3–4% in smokers[27].

The absorption and excretion of CO from the body occur relatively slowly; thus, exposure to elevated CO levels over short time periods will not result in a significant increase in the COHb level in the blood. Table 3 details the various health effects observed at different COHb levels. This table confirms that exposure to CO that results in a COHb level greater than ~2% should be avoided to protect the most vulnerable individuals in the population.

In order to protect the most vulnerable in society, a Norwegian expert group on air pollution[27] recommended maximum CO concentrations for different exposure times that will prevent COHb levels from exceeding 1.5%, taking into consideration endogenous CO formation (Table 4).

Table 4. Estimates of carbon monoxide (CO) levels in ambient air that will result in carboxyhaemoglobin (COHb) levels of 1.5%, including endogenous CO production[a]

Exposure time	CO concentration in air (mg/m³)		
	At rest	Moderate activity	Heavy work
15 min	170	80	52
30 min	86	42	29
1 h	48	24	18
8 h	11.5	9.2	9.2

[a]Data taken from Ref. 27

Exposure to CO on consumption of fresh meat treated with a CO gas mixture

Very little information exists in the literature on the exposure to CO following the consumption of meat that has been treated with CO gas. The inhalation of air containing CO at a level of 57 mg/m³ (the acceptable level in working environments in the USA) would provide a COHb level for a prolonged time period (hours) of at least 14 times that of the level reached temporarily on the consumption of 225 g of meat that had been packaged in CO at the saturation level for myoglobin[14]. In this estimate, it was assumed that the saturation of the meat myoglobin and haemoglobin was maximal and that the transfer of CO from the gastrointestinal tract to the blood was 100%. Consequently, even for such a 'worst-case' scenario, the treatment of meat with CO gas appears to contribute very little to COHb levels, relative to levels that are considered safe in the working environment. The exposure of beef to an atmosphere containing 1% CO for 3 d resulted in ~30% saturation of the meat myoglobin[28]. CO is lost from previously CO-treated meat during storage in the absence of CO, with a half-life of ~3 d. When the beef was cooked at 195°C, only 0.1 mg of CO remained per kg of meat. The loss of CO amounted to ~85%.

Comparison of CO exposure from air and the consumption of gas-treated meat

Data are very scarce, but comparisons still allow crude estimates to be made. An adult inhales ~10–20 m³ of air in 24 h (depending on their level of activity). This is equivalent to 0.42–0.84 m³/h (or 3.36–6.72 m³ in 8 h). In order to prevent a maximum COHb level in the blood of 1.5% being exceeded, the CO concentration in air for a 1-h period of moderate physical activity should not exceed 24 mg/m³, or 9.2 mg/m³ in 8 h (according to Table 4). In contrast, the consumption of meat that had been treated for 3 d in an atmosphere containing 1% CO yielded ~0.1 mg of CO per kg of meat on storage and cooking[28]. Based on these data, a comparison can be made from the two methods of exposure to CO, and is shown in Table 5.

Equilibrium between CO present in the atmosphere and the COHb concentration in blood is reached only after a considerable period of time (depending on the concentration and level of physical activity). Even in a 'worst-case' scenario, equilibration between the CO concentration in the gastrointestinal tract and blood will take time. Furthermore, the absorption of CO from the gastrointestinal tract into the blood will in all probability be less effective than the absorption of CO from the lungs, which are composed of tissues that are designed to facilitate gas exchange between the alveoli and the blood. Consequently, it is highly probable that the consumption of one meal of CO-exposed meat per day will not result in measurable increases in the COHb level in blood.

Toxicological evaluation of the use of CO as a packaging gas for meat

Unfortunately, the European Union (EU) has not evaluated CO for use as a packaging gas for meat. However, CO_2 and nitrous oxide (N_2O) have both been approved for use for extraction purposes, and it was considered unnecessary to adopt an acceptable daily intake (ADI) value for these gases in this application[29].

In order to avoid possible adverse health effects in those individuals who are the most susceptible, a Norwegian expert group on air pollution recommended maximum CO concentrations in ambient air that result in COHb levels not exceeding 1.5% (including endogenous CO production)[27]. Estimates detailed above indicat that, even assuming an improbable 100% absorption of CO from the gastrointestinal tract into the blood, the consumption of meat that has been treated with 1% CO will result in COHb levels that are negligible (approximately three orders of magnitude lower) compared with those resulting from exposure in the working environment to CO at an acceptable level. Consequently, it is highly improbable that CO exposure from meat packaged in an atmosphere containing up to 0.5% will represent a toxic threat to consumers through the formation of COHb.

Alternatives to the MAP of retail meat

Currently, the most commonly used MA for the retail packaging of meat contains O_2 at a high concentration in combination with CO_2, such as ~70% O_2/30% CO_2. The shelf life of meat in a high O_2 atmosphere in commercial practice, typically at temperatures of 6–8°C, is ~7 d, being limited both by microbiological spoilage and discolouration. Meat that is stored in a high O_2 concentration is often spoiled by bacteria such as *Brochothrix thermosphacta* and pseudomonads[30]. In MAs with a high concentration of O_2, the meat normally maintains its bright red oxymyoglobin colour for 4–7 d before the colour starts deteriorating to grey–brown, owing to the formation of metmyoglobin[18]. This length of time is often not considered to be sufficient to display and sell the product.

The use of MAs with a high concentration of CO_2, either alone or in combination with up to 70% N_2, would increase the microbiological shelf life of the meat compared with that of meat in a MA with a high O_2 concentration. The absence of O_2 together with the presence

of CO_2 retards microbiological growth. Unfortunately, the colour of meat packaged in MAs containing CO_2 is less satisfactory, being either purple or grey–brown due to the formation of deoxymyoglobin or metmyoglobin, respectively. The meat inevitably discolours when the O_2 concentration is low. Metmyoglobin formation can be avoided by maintaining O_2 concentrations <0.01–0.1% for beef[31] and <0.5% for pork[32]. These low O_2 levels, particularly for beef, are difficult to achieve in most commercial packaging operations, because a small amount of air will unavoidably be incorporated in the MAs of the packages. MAs with a high CO_2 concentration seem to be useful for retail packaging if a low concentration of CO is also included to stabilize myoglobin and the meat colour.

Table 5. Theoretical uptake of carbon monoxide (CO) in blood

Exposure method	CO intake in 1 h	CO intake in 8 h
Lungs (15 m³/d)	24 mg × 0.625 = 15.1 mg	9.2 mg × 5 = 46.0 mg
Meat (250 g, CO treated)	0.025 mg	0.025 mg

Vacuum packaging is commonly used for the bulk storage, transportation and export of meat. However, vacuum packaging has not proved to be a successful method for the retail packaging of meat, because of the purple deoxymyoglobin colour of the meat and the visible exudate that occurs in the packages[5,30]. Meat that is packaged in a vacuum cannot be presented in the bright red oxymyoglobin state, which depends on the presence of a high concentration of O_2[30,33], or in the cherry red carboxymyoglobin state, which requires CO to be included in the MA.

One of the objections that has been raised against the use of CO as a packaging gas is the potential hazard it might represent to workers in meat plants. Although the use of pure CO for mixing in the plant would certainly pose such a risk, the delivery of 1% CO in a mixture with 99% N_2, which has been the practice of gas suppliers to the Norwegian meat industry, is recognized by the health authorities to be a very safe handling procedure.

MAs that contain 60–70% O_2 must be handled carefully, because they are explosive gas mixtures. Strict safety regulations apply to explosive gas mixtures, increasing the costs of equipment and packaging operations. The benefits of a CO mixture is that it carries no risk of explosion and therefore does not increase handling costs.

Despite the long-term knowledge of the many advantages of the use of CO as a component of MAs for meat, CO mixtures have not been adopted to any great extent by the global meat industry. In many countries, including the USA and countries within the EU, CO is presently not permitted for use in the MAP of meat[3,34]. However, Norwegian food control authorities have not opposed the use of CO as a packaging gas at concentrations of up to 0.5%. As a member of the European Economic Agreement, Norway is expected to adapt gradually to EU food regulations, including those relating to gases for the packaging of foods. The Norwegian meat industry is therefore preparing an inquiry, to be directed at the Norwegian and EU food control authorities, for the continued use of CO in the MAP of red meats, which will be partly based on the toxicological evaluation described in this article.

Consumers may evaluate the shelf life of packaged meat on the basis of its colour. A possible negative aspect of using CO in the MAP of retail meat is concern that consumers might misjudge the quality of a product, because its true microbiological status may be masked by its stable, cherry red carboxymyoglobin colour[1]. However, consumers will be able to detect spoilage by the presence of off-odours. At the current low concentrations, <0.5%, CO *per se* seems to have no or only minor effects on bacteria and the shelf life of the meat. The combination of CO with a high concentration of CO_2, for example 60–70%, is necessary for microbiological control. Although MAP enables centralized packaging operations with quality control to be carried out, MAP alone cannot guarantee the shelf life of the product. Sufficient shelf life can be obtained only through the proper quality control of raw materials, production, packaging, chill chain and retail conditions.

Conclusions

Gas mixtures that contain a low concentration of CO, up to 0.5%, and a high concentration of CO_2, ~70%, have many advantages with respect to shelf life, colour stability, labour safety and costs. The use of CO at such concentrations does not present any toxic threat to consumers. Considering the benefits the Norwegian meat industry has experienced with CO gas mixtures over the past decade, potential exists for their wider application in the retail packaging of meat.

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The storage life of beef and pork packaged in an atmosphere with low carbon monoxide and high carbon dioxide

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Abstract

Ground beef, beef loin steaks and pork chops were packaged in modified atmospheres of 0.4% CO/60% CO_2/40% N_2 and 70% O_2/30% CO_2. In addition ground beef was packaged in clipped chub packs, beef loin steaks were vacuum packaged, and pork chops were packaged in an atmosphere of 60% CO_2/40% N_2 with each pack containing an O_2 absorber. The packs were stored in the dark at 4 or 8°C for up to 21 days. Meat in 0.4% CO/60% CO_2/40% N_2 had a stable bright red colour that lasted beyond the time of spoilage. The storage lives in this gas mixture at 4°C, as limited by off-odours, were 11, 14 and 21 days for ground beef, beef loin steaks and pork chops, respectively. The 70% O_2/30% CO_2 atmosphere resulted in an initially bright red to red colour of the meat, but the colour was unstable and off-odours developed rapidly. The off-odours probably were caused by *Brochothrix thermosphacta*, which grew in all meat types, or by pseudomonads in ground beef. Meat stored in chub packs, vacuum packs or 60% CO_2/40% N_2 with an O_2 absorber developed off-odours and microflora similar to those of meat in 0.4% CO/60% CO_2/40% N_2, but with less acceptable appearances. These results show that a low CO/high CO_2 atmosphere is effective for preserving retail-ready meat.

1. Introduction

The main reasons for modified atmosphere packaging (MAP) of red meats for retail sale are to prolong the microbiological shelf life and to maintain an attractive red colour of the product. Modified atmospheres (MA) usually consist of carbon dioxide (CO_2) for inhibiting microbiological growth, oxygen (O_2) for enhancing colour and, occasionally, nitrogen (N_2) as a filler. The most common gas mixture for retail-ready meat contains approximately 70% O_2 and 30% CO_2, and gives the product an extended shelf life compared to air (Gill, 1996). The shelf life and colour stability of meat stored in this gas mixture is still limited. To obtain a stable red colour for the meat, low concentrations (< 1%) of carbon monoxide (CO) can be introduced in the MA. Then, O_2 can be removed from the gas mixture and the concentration of bacteriostatic CO_2 can be increased. Anaerobic conditions extend the shelf life of meat considerably compared to air and O_2-enriched atmospheres (Gill & Molin, 1991). CO binds strongly to the meat pigment myoglobin to form stable carboxymyoglobin which has a cherry red colour (El-Badawi, Cain, Samuels, & Angelmeier, 1964). Low concentrations of CO have little effect on the microflora of meat (Clark, Lentz, & Roth, 1976; Gee & Brown, 1978; Luño, Beltrán, & Roncalés, 1998).

The Norwegian meat industry has for the past decade been using a gas mixture of approximately 0.3–0.5% CO, 60–70% CO_2 and 30–40% N_2 in retail-ready packages of beef, pork and lamb. Packages with this gas mixture now have a 50–60% share of the domestic, retail, red meat market. The technological, hygienic and toxicological aspects of using CO in MA for meat have recently been reviewed with the conclusion that CO used in concentrations up to 1% does not present a toxic hazard to the consumer (Sørheim, Aune, & Nesbakken, 1997a). However, CO may mask spoilage, because the stable cherry red colour can last beyond the microbiological shelf life of the meat (Kropf, 1980).

The inclusion of CO in MA for meat is controversial. CO is presently not allowed in MA for meat in the USA and in the EU (Cornforth, 1994; European Parliament and Council Directive, 1995). However, Norwegian food control authorities have up to now not opposed

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the use of up to 0.5% CO in MA for meat. This would change with an adoption of EU food regulations in Norway. Consequently, the Norwegian meat industry is seeking amendments of current EU food regulations relating to the use of CO in MAP of red meats. If the use of CO should be disallowed, other means of maintaining the long shelf life and the attractive red colour of the meat will have to be sought.

The aim of the present experiments was to compare a commercial Norwegian $CO/CO_2/N_2$ mixture with alternative gas mixtures and packaging methods for their effects on the off-odour, microflora and colour of ground beef, beef loin steaks and pork chops stored at 4 or 8°C for up to 21 days.

2. Materials and methods

2.1. Preparation of meat

2.1.1. Ground beef

Twenty cow and bull carcasses of Norwegian Red Cattle, which weighed on average 275 kg, were electrically stimulated with 90 V and were chilled using programmed air temperatures between 12 and −5°C. Two days after slaughter the carcasses were deboned, and trimmings with 14% fat were ground through a 4 mm plate. The batch of ground beef was divided into 500 g portions.

2.1.2. Beef loin steaks

Loins (*m. longissimus lumborum et thoracis*) with ultimate pH values below 5.8 were deboned from 25 bull carcasses of Norwegian Red Cattle. These carcasses, which weighed on average 275 kg, were stimulated, chilled and deboned the same way as the carcasses used in the preparation of ground beef. The loins were vacuum packaged and aged for 11 days at 3°C. Thereafter, the loins were cut into steaks 2.5 cm thick, and were randomly assigned to retail packs which each contained two steaks.

2.1.3. Pork chops

Thirty pig carcasses of Norwegian Land Race, which weighed on average 75 kg, were blast-chilled. Four days after slaughter, bone-in loins were removed and crust-frozen in liquid N_2 at −50°C for 20 min to facilitate cutting of chops. The chops, which were 1.6 cm thick, were randomly assigned to retail packs which each contained two chops.

2.2. Packaging

Ground beef, beef loin steaks and pork chops were packaged in 0.4% CO/60% CO_2/40% N_2 (CO mixture) and 70% O_2/30% CO_2 (high O_2). In addition, ground beef was packaged in clipped chub packs, beef loin steaks were vacuum packaged and pork chops were packaged in 60% CO_2/40% N_2 with one Ageless® FX-100 O_2 absorber (Mitsubishi Gas Chem. Co. Inc., Tokyo, Japan) in each pack (mixture with O_2 absorber).

The meat was packaged at a commercial meat plant within 2 h of grinding or cutting. Meat in the CO mixture, the high O_2 mixture and the mixture with O_2 absorber was packaged in an Ilapak Delta 2000 flow-packaging machine (Ilapak Machine Auto S.A., Grancia, Switzerland). The CO mixture was a blend of 1% CO/99% N_2 with 100% CO_2. The high O_2 mixture was used as a preblend. The mixture with O_2 absorber was a blend of 100% N_2 with 100% CO_2 (all gases, Hydrogas, Porsgrunn, Norway). The initial gas volume to meat weight ratio in the packs was approximately 1.5 to 1. The packs consisted of polyethylene trays (Færch Plast, Holstebro, Denmark) wrapped in Cryovac BDF 550 shrinking film (Cryovac, Milan, Italy) with an O_2 transmission rate of 19 $cm^3/m^2/24$ h/atm at 23°C and 0% RH. Chub packs of ground beef were packaged in a clipping machine (Poly-Clip, Frankfurt, Germany) using a red, fishingnet-patterned, polyethylene film (SFK, Vidovre, Denmark) with an O_2 transmission rate of 500 $cm^3/m^2/24$ h/atm at 23°C and 0% RH. Beef loin steaks were vacuum packaged in a Multivac 5100 thermo-forming machine (Multivac, Wolfertschwenden, Germany) using a terephtalate/polyethylene upper film and polyamide/polyethylene lower film with O_2 transmission rates of 10 and 16 $cm^3/m^2/24$ h/atm at 23°C and 0% RH, respectively (Danisco, Horsens, Denmark).

2.3. Storage and sampling of meat

Five samples were collected from the ground beef batch, beef loins and pork loins before packaging, for pH measurements and microbiological analyses.

The packaged meat was stored in dark chilling rooms at 4 ± 0.5 or 8 ± 0.5°C for up to 21 days at least until off-odours developed. Five packs were removed per product, packaging method, storage temperature and sampling day after the following storage times:

- ground beef: 2, 4, 6, 8 or 11 days;
- beef loin steaks: 3, 7, 10 or 14 days; and
- pork chops: 3, 7, 10, 14, 17 or 21 days.

2.4. Gas analyses

The atmospheres of packs with MA were analysed for O_2 and CO_2 immediately after packaging (approximately every tenth pack) and at sampling (all packs). O_2 was determined using a Toray LC 700-F gas analyser (Toray Engineering, Osaka, Japan) and CO_2 using a Toray PG-100 gas analyser (Toray). The threshold levels for the O_2 and CO_2 analyses were 0.05 and 1%, respectively. Gas samples of 10 cm^3 were removed with a syringe through selfsealing patches on the packs.

2.5. pH

The pH measurements were made directly in the meat with an Ingold Xerolyt gel electrode (Mettler-Toledo A.G., Greifensee, Switzerland).

2.6. Odour

The meat was evaluated for odours by a three member trained panel between 0.5 and 1 min after opening of the packs. The off-odour scale used was: 1 = none, 3 = slight and 5 = extreme. Scores of 3 or below were considered acceptable.

2.7. Microbiology

Ten gram meat samples were collected from portions of the ground beef, and diluted in 90 g peptone water. A sample 25 cm^2 and 2–3 mm thick was removed from the surface of each beef loin or steak and pork loin or chop with a scalpel, and diluted in 100 ml peptone water. Each sample was macerated in a Stomacher for 1 min. Serial 10-fold dilutions of each Stomacher fluid were prepared, and 20 µl volumes of appropriate dilutions were plated in duplicate on the following media:

- plate count agar (PCA; Difco, Difco Laboratories, Detroit, MI, USA) for total viable counts;
- de Man, Sharpe and Rogosa agar (MRS; Oxoid, Unipath Ltd., Basingstoke, Hampshire, UK) adjusted to pH 5.7 for lactic acid bacteria (de Man, Rogosa, & Sharpe, 1960);
- streptomycin thallous acetate actidione agar base (STAA; CM 881 with selective supplement SR 151; Oxoid) for *Brochothrix thermosphacta*;
- pseudomonads agar base (CFC; CM 559 with selective supplement SR 103; Oxoid) for pseudomonads;

In addition, 1 ml portions of appropriate dilutions were plated in duplicate on petrifilm coliform count plates (3M Microbiology Products, St. Paul, MN, USA) for enumeration of coliforms and *Escherichia coli*.

Plates of PCA, MRS, STAA and CFC were incubated at 20°C for four days, and petrifilm plates at 30°C for up to 2 days, all aerobically. Counts were expressed as colony forming units (CFU) per g or cm^2.

2.8. Colour

A six-member trained panel evaluated the colour of the meat in intact packs under 1200 ± 200 lux Warmton Lumilux L36W/31 yellow–white light (Osram, Drammen, Norway). The colour was assessed on a scale where 1 = bright red (ground beef and beef loin steaks) or light bright red (pork chops), 2 = red (ground beef and beef loin steaks) or light red (pork chops), 3 = slightly brown, grey or green, 4 = moderately brown, grey or green and 5 = extremely brown, grey or green (National Live Stock and Meat Board, 1991).

A Minolta Chroma Meter CR-300 (Minolta Camera Co., Osaka, Japan) with 8 mm viewing port and illuminant D_{65} was used for measuring CIE a^* values (redness). The colour was measured directly at the meat surface within 1 min of opening of each pack.

Ground beef in chub packs was not included in the colour analyses because the red packaging film hides the colour of the product. With pork chops, the colour of only the *m. longissimus lumborum et thoracis* was analysed.

2.9. Statistics

Analysis of variance by Tukey's multiple comparisons test was performed using the Systat programme, version 6 (Systat Inc., Evanston, IL, USA).

3. Results

3.1. Gas composition

The initial O_2 concentrations in packs with the CO mixture and the mixture with O_2 absorber were all below 0.5% immediately after packaging. O_2 was not detected in these packs after 2 or 3 days storage. The level of O_2 in packs of high O_2 was reduced from the initial 70 to 60–65% during storage for up to 21 days. Concentrations of CO_2 in the packs were generally reduced by one fifth after 2 or 3 days storage, and were then stable (data not shown).

3.2. Storage life of ground beef

The time to develop off-odours was 2 to 3 days longer for ground beef stored in the CO mixture and in chub packs than in high O_2, and it was 4 or 5 days longer at 4 than at 8°C for all three packaging methods (Table 1). In high O_2, the total viable counts increased faster and were higher ($p < 0.01$) than for the other two types of packaging after 2 days at either 4 or 8°C [Fig. 1(a)]. The total viable counts were more than 90% lactic acid bacteria (data not shown). The high numbers of lactic acid bacteria in ground beef, up to approximately $\log_{10}$ 8 CFU/g, caused a decrease in the pH value from the initial 5.7 to 5.2 after 6 days when the meat was stored in the CO mixture or chub packs at 8°C (data not shown). At 4°C, the pH value was reduced to 5.5 after 11 days in both those packaging systems. The numbers of *B. thermosphacta* increased, in meat in high O_2 [Fig. 1(b)]. In meat in high O_2 the numbers of pseudomonads increased up to approximately $\log_{10}$ 7 CFU/g, but only to $\log_{10}$ 5 and 6 CFU/g in

meat in the CO mixture or chub packs, respectively (data not shown).

Ground beef in the CO mixture had a stable bright red colour, as shown by both the low colour scores and the high a^* values [Fig. 1(c) and (d)]. Meat in high O_2 was significantly less red ($p < 0.05$) than meat in the CO mixture, with higher colour scores and lower a^* values at day 2 and at later storage times at both 4 and 8°C. The colour of meat in high O_2 deteriorated with time, significantly faster ($p < 0.01$) at 8 than at 4°C.

Table 1
Time for development of off-odours in different types of meat in various packagings at storage temperatures of 4 or 8°C

Product	Packaging[a]	Time of off-odour detection (days)	
		4°C	8°C
Ground beef	CO mixture	11	6
	High O_2	8	4
	Chub packs	11	6
Beef loin steaks	CO mixture	14	7
	High O_2	10	7
	Vacuum packs	14	7
Pork chops	CO mixture	21	14
	High O_2	14	7
	Mixture with O_2 absorber	17	10

[a] CO mixture = modified atmosphere of 0.4% CO/60% CO_2/40% N_2; High O_2 = modified atmosphere of 70% O_2/30% CO_2; Mixture with O_2 absorber = modified atmosphere of 60% CO_2/40% N_2 with an O_2 absorber in the pack.

3.3. Storage life of beef loin steaks

At 4°C, off-odours developed 4 days later in beef loin steaks in the CO mixture and in vacuum packs than in high O_2 (Table 1). At 8°C, no differences in the development of off-odours were observed. Off-odours developed 4 to 7 days earlier in meat at 8 than at 4°C. The type of packaging did not significantly affect ($p < 0.05$) the total viable counts on the meat, but the counts were significantly higher ($p < 0.01$) at 8 than at 4°C after both 3 and 7 days of storage [Fig. 2(a)]. The numbers of *B. thermosphacta* were less than $\log_{10}$ 4 CFU/cm^2 in meat in all types of packaging at all times, but were significantly higher ($p < 0.05$) on meat in high O_2 at 7 and 10 days than on meat in the CO mixture and in vacuum packs at equivalent times [Fig. 2(b)]. The numbers of pseudomonads did not exceed $\log_{10}$ 3.5 CFU/cm^2 at any sampling time, and were not significantly affected ($p > 0.05$) by the type of packaging or the storage temperature.

The colour of the beef loin steaks in the CO mixture was stable bright red throughout storage at both 4 and 8°C, as shown by the low colour scores and high a^* values [Fig. 2(c) and (d)]. Steaks in high O_2 were also bright red with high a^* values at day 3, but these steaks discoloured gradually between days 3 and 10, significantly faster ($p < 0.05$) at 8 than at 4°C. Meat in vacuum packs was slightly discoloured with low a^* values throughout storage. The colour scores and a^* values of vacuum packaged steaks were not significantly affected ($p > 0.05$) by the storage temperature.

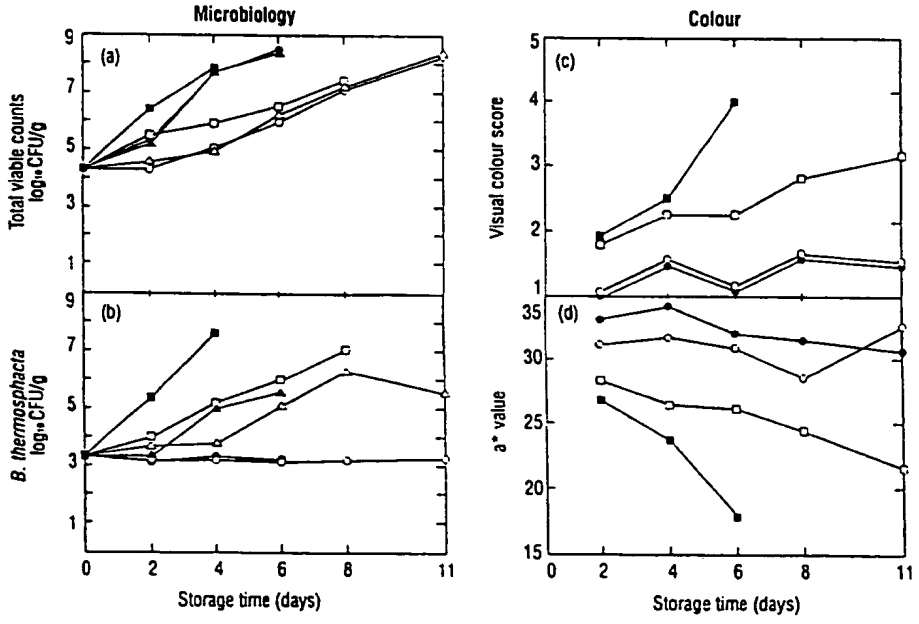

Fig. 1. Mean values ($n = 5$) for (a) total viable counts, (b) numbers of *Brochothrix thermosphacta*, (c) visual colour scores and (d) CIE a^* values for ground beef stored in 0.4% CO/60% CO_2/40% N_2 at 4°C (○) or 8° C ( ), in 70% O_2/30% CO_2 at 4°C (□) or 8°C (■), or in chub packs at 4°C (△) or 8°C (▲). Colour was assessed on a scale where 1 = bright red and 5 = extremely discoloured.

3.4. Storage life of pork chops

For pork chops, off-odours developed more slowly in meat in the CO mixture than in meat in the mixture with O_2 absorbers or in high O_2 (Table 1). Off-odours were detected 7 days earlier at 8 than at 4°C for chops in each type of packaging. The type of packaging did not affect the total viable counts on the pork chops [Fig. 3(a)]. However, the counts were greater on meat stored at 8 than at 4°C. The numbers of *B. thermosphacta* on chops in high O_2 were significantly higher ($p < 0.01$) than on chops in the CO mixture or in the mixture with O_2 absorbers after 7 days at 8°C or 10 days at 4°C, and reached approximately $\log_{10} 6$ CFU/cm^2 [Fig. 3(b)]. The numbers of pseudomonads did not exceed $\log_{10} 3$ CFU/cm^2 on any of the pork chops.

The colour of pork chops in the CO mixture was light bright red with high a^* values throughout storage [Fig. 3(c) and (d)]. Chops in high O_2 were red at day 3, but discoloured during storage, significantly faster ($p < 0.05$) at

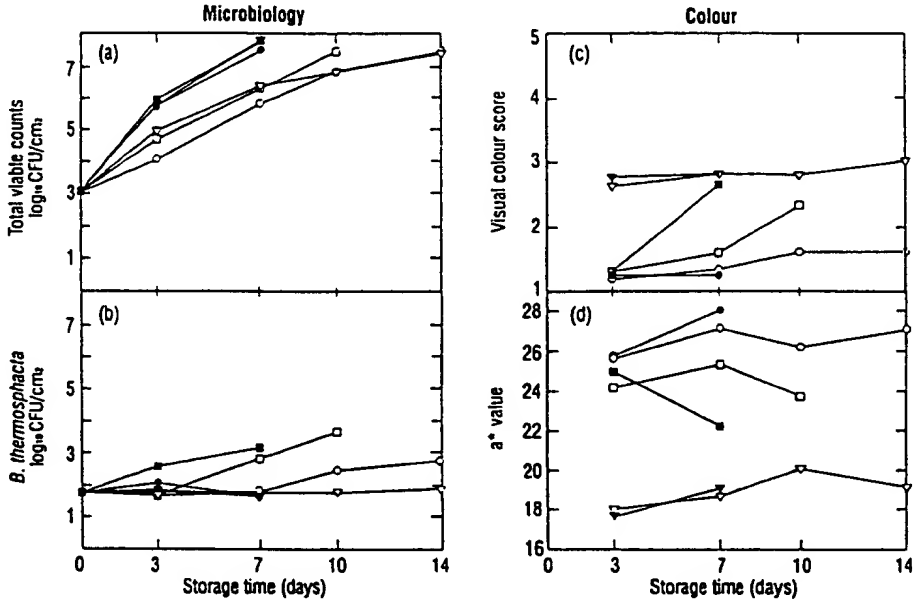

Fig. 2. Mean values ($n = 5$) for (a) total viable counts, (b) numbers of *Brochothrix thermosphacta*, (c) visual colour scores and (d) CIE a^* values for beef loin steaks stored in 0.4% CO/60% CO_2/40% N_2 at 4°C (○) or 8°C (●), in 70% O_2/30% CO_2 at 4°C (□) or 8°C (■), or in vacuum packs at 4°C (▽) or 8°C (▼). Colour was assessed on a scale where 1 = bright red and 5 = extremely discoloured.

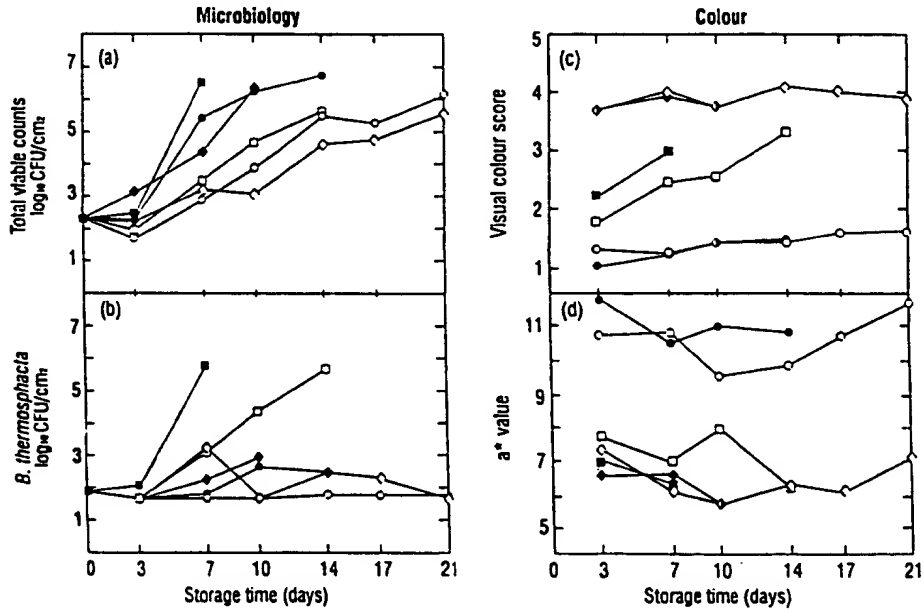

Fig. 3. Mean values ($n = 5$) for (a) total viable counts, (b) numbers of *Brochothrix thermosphacta*, (c) visual colour scores and (d) CIE a^* values for pork chops stored in 0.4% CO/60% CO_2/40% N_2 at 4°C (○) or 8° C (●), in 70% O_2/30% CO_2 at 4°C (□) or 8°C (■), or in 60% CO_2/40% N_2 with O_2 absorbers at 4°C (◇) or 8°C (◆). Colour was assessed on a scale where 1 = light bright red and 5 = extremely discoloured.

8 than at 4°C. Approximately 75% of the chops in high O_2 had black back bones at the time of sampling. Chops in the mixture with O_2 absorbers were moderately discoloured from day 3 to the end of storage. These chops had a^* values similar to those of chops in high O_2.

4. Discussion

4.1. Off-odour and microflora

The shelf life of the meat, as determined by the time to develop off-odours, was influenced by the packaging method, the storage temperature and the initial microbiological load on the meat. Storage of meat in the CO mixture, in vacuum packs or in chub packs gave the longest shelf lives. Meat stored in high O_2 generally developed off-odours 2–7 days earlier at 4 or 8°C than meat packaged in the other gas mixtures or by the other methods.

The differences in the rates of development of off-odours, as affected by the packaging method, were seldom related to any differences in numbers of total viable counts. However, the development of off-odours from the three meat types, especially ground beef and pork chops in high O_2, coincided with the attainment of high numbers of *B. thermosphacta*. For ground beef, storage in the CO mixture retarded growth of *B. thermosphacta* even more than storage in chub packs. At chill temperatures above 1°C, *B. thermosphacta* often causes spoilage of meat stored in high O_2 atmospheres (Dainty & Mackey, 1992). High concentrations of CO_2, removal of O_2 and low storage temperature inhibit the growth of *B. thermosphacta* (Gill, 1996; Nissen, Sørheim, & Dainty, 1996). Pseudomonads probably contributed to the off-odours of ground beef. Meat in high O_2 is often spoiled by *Pseudomonas* spp., but the growth of pseudomonads is retarded under anaerobic conditions (Dainty & Mackey, 1992; Gill, 1996). A shift in the metabolism of lactic acid bacteria under aerobic conditions can also produce off-odours (Nissen et al., 1996). In the present experiments, the numbers of coliforms or *E. coli* did not exceed $\log_{10}$ 3 CFU/g or cm^2 in any samples. Therefore, those organisms probably did not contribute to off-odours.

For pork chops, the effect of CO on the microflora can be evaluated because the gas compositions of the CO mixture and of the mixture with O_2 absorber were identical, except for the inclusion of 0.4% CO in the former. Although a 4 day increase in the time to develop off-odours was observed with the CO mixture, there was no significant reduction in the microbiological counts. Luño et al. (1998) used 1% CO in high O_2 atmospheres and noted a delay in the onset of off-odours without any reduction in the numbers of psychrotrophic bacteria. However, Clark et al. (1976) found that the addition of 0.5-10% CO to N_2 atmospheres reduced the number of psychrotrophic bacteria and increased the odour shelf life of beef. For example, 1.0% CO in 99% N_2 increased the time to develop off-odours at 5°C from 18 to 24 days. The lack of such an effect of CO on bacteria in our experiments may be due to the use of 60% CO_2 overshadowing any effect of CO.

The use of CO makes it possible to dispense with O_2 and so to increase the CO_2 concentration in a MA to about 60%. Our data suggest that 0.4% CO probably has little or no direct effect on the growth of bacteria. Other studies have shown that increasing the CO_2 concentration from 20 to 100% increases the bacteriostatic effect of the gas, but the efficiency is highly dependent on low storage temperatures (Gill & Molin, 1991; Nissen et al., 1996). The high CO_2 concentration and absence of O_2 in the CO mixture will favour the growth of lactic acid bacteria, which usually cause a mild form of spoilage only late in the development of the spoilage flora (Gill, 1996).

The present experiments were performed at acceptable and abusive storage temperatures to assess the effects of temperatures commonly encountered in the distribution and sale of retail-ready meat. The storage temperature strongly affected the rates of growth of microflora and the time to develop off-odours. Consequently, independently of the packaging method, the shelf life of meat can be considerably extended by maintaining low temperatures in the chill chain (Gill & Molin, 1991; Nissen et al., 1996).

4.2. Colour

The CO mixture gave a stable bright or light bright red colour with consistent high a^* values for all three products, irrespective of the storage temperature. The initial level of residual O_2, up to 0.5%, did not adversely affect the visual scores and instrumental values for the colour of meat stored in the CO mixture.

CO binds to myoglobin and forms cherry red carboxymyoglobin (El-Badawi et al., 1964). This pigment is spectrally similar to the bright red oxymyoglobin which normally develops at the surface of fresh meat in air. Carboxymyoglobin is less readily oxidized to brown metmyoglobin than is oxymyoglobin, because of the strong binding of CO to the iron-porphyrin site on the myoglobin molecule (Lanier, Carpenter, Toledo, & Reagan, 1978; Wolfe, 1980). Consequently, CO in concentrations of 0.5–2.0% enhances and stabilizes a bright red colour of meat (Kropf, 1980; Sørheim et al., 1997a). In a recent study, 1% CO in combination with 24 or 70% O_2 stabilized the colour of beef by reduced formation of metmyoglobin after storage at 1°C for up to 29 days (Luño et al., 1998). However, in a study of beef stored in a MA of 2% CO/78% CO_2/20% N_2, the colour of the meat was characterized as "too artificial" by

a sensory panel (Renerre & Labadie, 1993). From our studies and experience from the Norwegian meat industry, 0.4% CO seems sufficient to produce a stable, attractive, bright red colour of meat.

All three meat types stored in high O_2 were bright red to red with high a^* values early in the storage periods, approaching the colour of meat in the CO mixture. As the microbiological counts of meat in high O_2 increased, the colour deteriorated, faster at 8 than at 4°C. Meat stored in a MA of high O_2 develops a thicker layer of oxymyoglobin than meat stored in air (Renerre & Labadie, 1993). However, the oxymyoglobin gradually oxidizes to metmyoglobin, and the oxidation is faster at higher temperatures.

For cut bone, haemoglobin released from disrupted red blood cells in the marrow will accumulate at the surface and ultimately become black after the bone has been exposed to air or O_2 (Gill, 1996). Although bone blackening was not considered in the present visual colour evaluation, it can negatively affect the saleability of bone-in meat at retail display. The cut bones of pork chops stored in high O_2 blackened during storage, but this discoloration was not observed on bones in the CO mixture and the mixture with O_2 absorbers.

Beef loin steaks stored in vacuum packs were slightly discoloured with low a^* values at both 4 and 8°C. In these packs, meat juices were observed between the upper and lower films, but that did not influence the colour evaluations.

O_2 absorbers in packs with high CO_2 facilitate the removal of residual O_2 and maintain atmospheres free of O_2 during storage (Smith, Abe, & Hoshino, 1995). Low levels of residual O_2, above 0.01–0.15% for beef and 0.5–1.0% for pork, will inevitably discolour the meat (Penney & Bell, 1993; Gill, 1996; Sørheim et al., 1997b). When no CO is present in an O_2 depleted MA, it is essential to remove the residual O_2 as fast and completely as possible to avoid formation of metmyoglobin. In these experiments, pork chops stored in the gas mixture with O_2 absorbers were moderately discoloured during the whole storage period at 4 or 8°C. Despite the obvious visible differences, these chops had similar a^* values to the chops in high O_2. The discoloured surface made the chops unfit for sale, even in the early stage of storage. The present findings contrast with previous results, where the colour of porcine *m. longissimus thoracis et lumborum* was significantly improved by using O_2 absorbers in MAs of CO_2 with residual O_2 (Sørheim et al., 1997b). The present discoloration could be caused by incomplete use or function of the absorbers (Gill, 1996).

4.3. Benefits and disadvantages of a MA with low CO/high CO_2

An objection raised against using CO as a small component of a MA for retail-ready meat is the possibility that the colour stability can exceed the microbiological shelf life, with the risk of masking spoilage of the meat (Kropf, 1980). Therefore, the consumer must evaluate the microbiological condition of meat in a CO mixture by off-odours. When a MA with CO is applied commercially, it is important to have a proper control of the hygienic condition of the meat raw materials and the chill chain temperatures.

CO used in concentrations below 1.0% does not present any hazard to the consumer, because consumption of meat packaged in such concentrations of CO will result in only negligible levels of carboxyhaemoglobin in the blood of consumers (Sørheim et al., 1997a). By delivering CO in a 1% mixture with 99% N_2, which is the practice of Norwegian gas suppliers, CO is considered safe for use in the working environment. Other MAs with high levels of O_2, up to 70%, must be regarded as explosive gas mixtures, which must be used with appropriate precautions for safety (Luño et al., 1998).

The suitability of gas mixtures and packaging methods for red meats for retail display depends on their ability to both reduce spoilage and stabilize colour. Gas mixtures with low concentrations of CO and high concentrations of CO_2 provide a combination of a long microbiological shelf life and a stable, bright red colour of meat. Meat packaged in a MA with high O_2 can achieve an initial bright red colour, but the microbiological shelf life and the colour stability are both considerably lower than those of meat in the CO mixture. Using CO eliminates the need to have O_2 as a component of the MA. Other MAs and packaging methods, like high CO_2 with O_2 absorbers, chub packs and vacuum packs may give a shelf life comparable to that of the CO mixture, but with a less acceptable colour or appearance of the meat. Thus, there appears at present to be no fully satisfactory alternative to the CO mixture used in packaging of retail-ready red meats in Norway.

Acknowledgements

The financial support of this study from the Research Council of Norway is highly appreciated. Vestfold-Buskerud Slakteri A/L, Sem and Hydrogas AS Utviklingssenter, Porsgrunn, are greatly thanked for packaging of the meat. We appreciate the gift of Ageless® O_2 absorbers from Cryovac Europe, Norderstedt, Germany. The technical staff and Per Lea (statistics) at MATFORSK are thanked for their skilful assistance in the study.

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UPDATE ON MODIFIED ATMOSPHERE PACKAGING OF MEAT

Cologn , Germany, 22 F bruary 2001

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The market share of pre-packaged retail meat in modified atmospheres in Norway is **60 %**

Due to
- structure of the retail market
- structure of the meat industry
- packaging with a gas mixture containing low levels of carbon monoxide (CO)

WHY SO MUCH MAP OF MEAT?

1. **Benefits for the food stores**
   - less space, handling and staff resulting in reduced costs
   - better quality, shelf-life and safety

2. **Benefits for the meat industry**
   - centralised and efficient packaging
   - better quality control
   - marketing of own trademarks

3. **Developments** in gas mixtures, packaging films, machinery and distribution concepts

4. **Traceability** for the meat is improved

5. **Meat** is a relatively **expensive** food

THE NORWEGIAN MEAT MARKET

4 big food store chains control 95 % of the food sale

1300 soft discount food stores have 45 % of the sale
- low prices and small staff
- 1500 –2500 goods maximum
- no manual fresh meat departments
- require case-ready pre-packaged meat

Long transportation, time-consuming distribution

Meat and meat products are expensive

Annual meat consumption +60 kg per person (predominantly beef and pork)

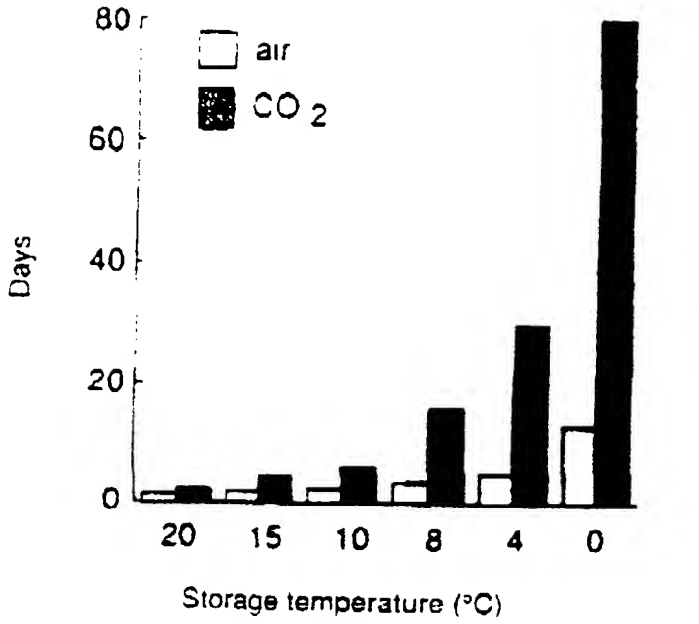
Almost no import and export, more competition expected

Gas mixtures for meat

In Europe, high O_2 mix, appr.:
70-80 % O_2 + 20-30 % CO_2

In Norway, CO mix, appr. :
0.3-0.5 % CO + 60-70 CO_2 + 30-40 % N_2

CO is allowed in Norway, but not in the EU or USA



Time (days) for spoilage flora to grow to $10^6/cm_2$ on pork stored at different temperatures in air and 100 % CO_2

Molin (1989)

MICROBIOLOGICAL SHELF LIFE OF MAP MEAT

Hygiene
- slaughtering
- deboning
- processing and packaging

Modified atmosphere packaging
- concentration and volume of CO_2
- absence of O_2

L w temp ratures and consistent chill chain

GAS MIXTURE WITH LOW LEVEL OF CO

- CO concentrations < 0.5 %
- stable, bright red colour of meat
- no or small antimicrobiological effect *per se* of CO
- delivered to the plants in a 1 % CO/ 99 % N_2 mixture, then blended with CO_2
- the low CO/ high CO_2 mixture is not explosive
- no toxic hazard to workers in packaging plants
- no toxic hazard to consumers

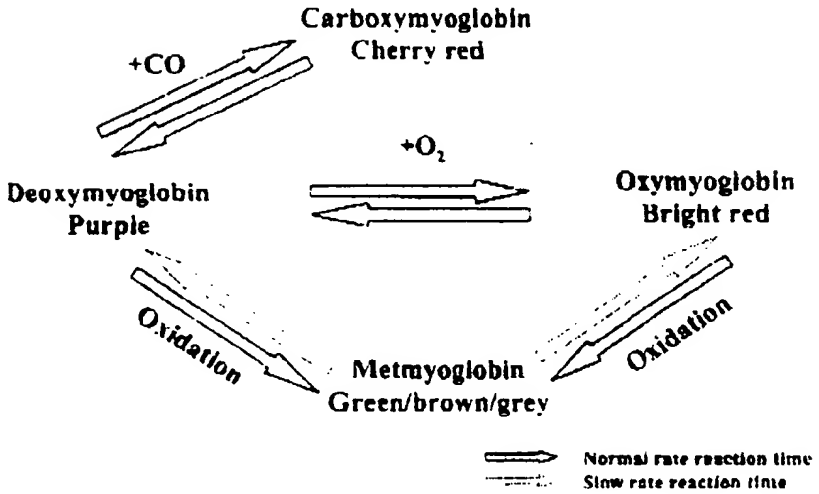
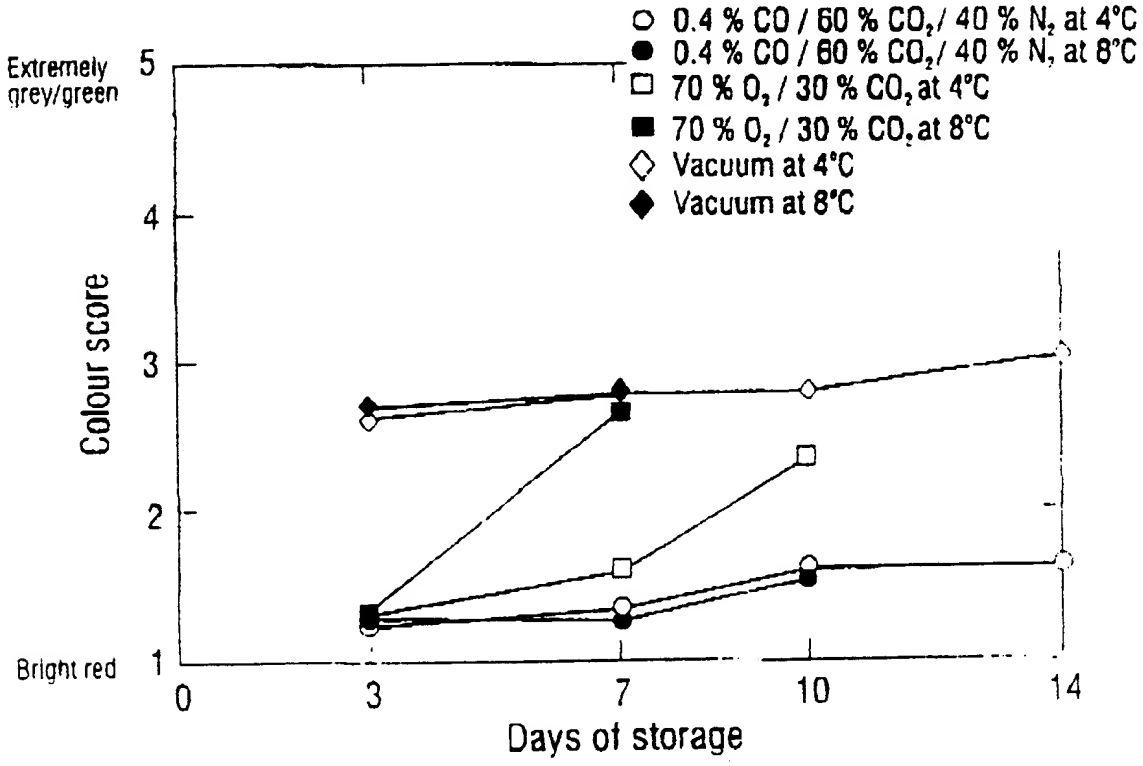


Figure 1. The colour of meat related to different forms of the pigment myoglobin.

various packagings at storage temperatures of 4 or 8°C

Product	Packaging[a]	Time of off-odour detection (days)	
		4°C	8°C
Ground beef	CO mixture	11	6
	High O_2	8	4
	Chub packs	11	6
Beef loin steaks	CO mixture	14	7
	High O_2	10	7
	Vacuum packs	14	7
Pork chops	CO mixture	21	14
	High O_2	14	7
	Mixture with O_2 absorber	17	10

[a] CO mixture = modified atmosphere of 0.4% CO/60% CO_2/40% N_2; High O_2 = modified atmosphere of 70% O_2/30% CO_2; Mixture with O_2 absorber = modified atmosphere of 60% CO_2/40% N_2 with an O_2 absorber in the pack.



Visual colour evaluation of beef loin steaks stored for 14 days

RETAIL MEAT PACKAGING. CONCLUSIONS:

Carb n mon xid gas mixture
- safe for the consumer
- safe for the plant workers
- stable, bright red colour
- long microbiolgical shelf life (high CO_2, absence of O_2)
- better safety against some pathogenic bacteria
- low rate of spoiled products, saving costs
- but, colour stabillty can last beyond shelf life thus potentially masking spoilage

High oxygen gas mixture
- short to medium shelf life
- initail red colour, but relatively poor colour stability

Other packaging methods (vacuum, skin-packs, oxygen absorbers, master-packs), in general
- long shelf life
- may have less acceptable colour or appearance
- mav include extra handling in the stores

Consumer test of retail mea

	Score*
Ground beef	
High O_2	3.7
CO mixture	3.7
Casings	2.5
Beef loin steaks	
High O_2	4.0
CO mixture	4.2
Vacuum	2.9
Pork chops	
High O_2	3.6
CO mixture	4.6
O_2 absorbers	1.9

125 participants. June 1996
* Scale:
1 - will certainly not buy, 5 - will certainly buy

CONTINUED AND EXTENDED USE OF CO?

EU allows
- carbon dioxide
- nitrogen
- oxygen
- argon, hellum and dinitrogen oxide
- but not carbon monoxide

Label requirement "Packaged in a protective atmosphere"

Temporary permission to use CO in concentrations below 0.5 % in Norway

The Norwegian meat industry has applied to domestic and EU food control authorities for continued use of CO < 0.5 %

The application is supported by meat trade organisations in many European countries

Re: Carbon monoxide gas treated frozen tuna

howgate (*phowgate@rsc.co.uk*)
Sun, 28 Feb 1999 12:05:50 -0000

- **Messages sorted by:** [date][thread][subject][author]
- **Next message:** Liz Brown: "Re: Carbon monoxide gas treated frozen tuna"
- **Previous message:** Pamela Tom: "Re: Carbon monoxide gas treated frozen tuna"
- **Maybe in reply to:** Al Arkan Trading: "Carbon monoxide gas treated frozen tuna"
- **Next in thread:** Liz Brown: "Re: Carbon monoxide gas treated frozen tuna"

Subject: carbon monoxide in packaged fish.

Arkan Trading wrote on 27 February:

"I have recently heard about carbon monoxide gas treated tuna in the form of vacuum packed tuna loins. Can anyone comment on the effect of carbon monoxide gas on humans? Is it acceptable according HACCP norms ?"

It would have been useful if anonymous correspondent from Arkan Trading had been a bit more specific about how they came about this information, and made clearer if they really meant vacuum packed tuna, MAP tuna, or frozen, packaged or not, tuna as the heading has it.

I believe tuna and salmon have been packaged as MAP products with the addition of carbon monoxide in the gas mix, but I do not know if this has been on a commercial basis. The question of the use of CO with fish products was put to me a few months ago and I looked at the literature, particularly reviews, on MAP and did not come across any mention of use of CO in fish products other than aside in a report by the UK MAFF Advisory Committee on the Microbiological Safety of Food, 'Report on Vacuum Packaging and Associated Processes' to the use CO for maintaining the red stripe of salmon, but no references are cited. Of course that does not mean it has not been used, even if only on a trial basis. It has been at least investigated for red meat products. It gives the meat a pink colour which is thought to be desirable. There is a review of this by Sorheim, O., Aune, T, & Nesbakken,T. Technological, hygienic and toxicological aspects of carbon monoxide used in modified-atmosphere packaging of meat, Trends in Food Science & Technology, 1997, 8, 307-312. The review refers to meat being packaged in gas mixtures containing 60-70% carbon dioxide, 30-40% nitrogen, and less than 0.5% CO. The authors concluded there was no health risk to consumers of meat packaged in this mixture.

Whether or not CO in packaged meats or fish presents a risk to health, food regulations in some countries will forbid, or at least, not permit, its use. The EU Directive on food additives (Council Directive No 95/2/EC of 20 February 1995 on 'food additives other than colours and sweeteners'),does not list CO as a permitted additive so the use of CO in packaged fish would not be permitted in the EU. I believe its use for

meat/fish products is not permitted in the USA, (though its use for vegetable products is), but perhaps someone from FDA would state what the position is.

Peter Howgate

- **Next message:** Liz Brown: "Re: Carbon monoxide gas treated frozen tuna"
- **Previous message:** Pamela Tom: "Re: Carbon monoxide gas treated frozen tuna"
- **Maybe in reply to:** Al Arkan Trading "Carbon monoxide gas treated frozen tuna"
- **Next in thread:** Liz Brown: "Re: Carbon monoxide gas treated frozen tuna"

Re: Carbon monoxide gas treated frozen tuna

Ralph Boragine (*rboragine@seafoodrus.org*)
Mon, 01 Mar 1999 07:08:27 -0500

- **Messages sorted by:** [date][thread][subject][author]
- **Next message:** Pamela Tom: "Electronic Data Loggers"
- **Previous message:** Cristianini, M.: "Re: CRAB CORE TEMPERATURE"

This is a multi-part message in MIME format.
----------591216EA653A449A92A43F77
Content-Type: text/plain; charset=us-ascii
Content-Transfer-Encoding: 7bit

Liz,
The response to date from the FDA is we don't:
1.) Have Staff
2.) Don't see the problem.
They FDA has procrastinated for nearly 6 months with our congressional folks.
Ralph Boragine

Liz Brown wrote: 2/25/99

> *The subject came up with apparent interest at the recent Pacific Fisheries*
> *Technologist meeting. Following is my understanding of the situation of CO use*
> *in the U.S. I would appreciate any corrections.*
>
> *CO continues to be used in tuna processing in Hawaii to enhance color*
> *retention. There is interest among mainland processors as well.*
>
> *Processors argue that CO is one of several compounds added during the normal*
> *smoking process and therefore should not considered hazardous nor considered an*
> *additive.*
>
> *The stance the FDA is likely to take will be that CO treatment is an attempt to*
> *mislead the consumer and will therefore be considererd economic adulteration*
> *unless labeled accordingly. The FDA is currently working on a rapid method of*
> *identifying products that have been CO treated.*
>
> *I look forward to hearing the FDA response.*
>
> --
> *Liz Brown*
> *Seafood Technology Program*
> *Sheldon Jackson College*
> *http://sj-alaska.edu*
> *801 Lincoln Street*
> *Sitka, Alaska 99835*
> *907-747-2554*
> *lbrown@sj-alaska.edu*

----------591216EA653A449A92A43F77
Content-Type: text/x-vcard; charset=us-ascii; name="vcard.vcf"
Content-Transfer-Encoding: 7bit
Content-Description: Card for Ralph Boragine
Content-Disposition: attachment; filename="vcard.vcf"

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fn: Ralph Boragine
n: Boragine;Ralph
org: RI Seafood Council/American Seafood Institute
adr: 212 Main Street, Suite 3;;;Wakefield;Rhode Island;02879;USA
email;internet: rboragine@seafoodrus.org
tel;work: 401-783-4200
tel;fax: 401-789-9727
x-mozilla-cpt: ;0
x-mozilla-html: FALSE
version: 2.1
end: vcard

----------591216EA653A449A92A43F77--

- **Next message:** Pamela Tom: "Electronic Data Loggers"
- **Previous message:** Cristianini, M.: "Re: CRAB CORE TEMPERATURE"

Vegetable Information
University of California - Vegetable Research and Information Center

POSTHARVEST HANDLING SYSTEMS: MINIMALLY PROCESSED FRUITS AND VEGETABLES

"Minimally processed" horticultural products are prepared and handled to maintain their fresh nature while providing convenience to the user. Producing minimally processed products involves cleaning, washing, trimming, coring, slicing, shredding, and so on. Other terms used to refer to minimally processed products are "lightly processed," "partially processed," "freshprocessed," and "preprepared."

Minimally processed fruits and vegetables include peeled and sliced potatoes; shredded lettuce and cabbage; washed and trimmed spinach; chilled peach, mango, melon, and other fruit slices; vegetable snacks, such as carrot and celery sticks, and cauliflower and broccoli florets; packaged mixed salads; cleaned and diced onions; peeled and cored pineapple; fresh sauces; peeled citrus fruits; and microwaveable fresh vegetable trays.

Whereas most food processing techniques stabilize the products and lengthen their storage and shelf life, light processing of fruits and vegetables increases their perishability. Because of this and the need for increased sanitation, preparation and handling of these products require knowledge of food science and technology and postharvest physiology.

Growth in demand has led to increased marketing of fresh horticultural products in lightly processed form. An industry dedicated to this type of food processing has been established, and the National Association of Fresh Produce Processors was recently formed.

Physiological Responses

Minimal processing generally increases the rates of metabolic processes that cause deterioration of fresh products. The physical damage or wounding caused by preparation increases respiration and ethylene production within minutes, and associated increases occur in rates of other biochemical reactions responsible for changes in color (including browning), flavor, texture, and nutritional quality (such as vitamin loss). The greater the degree of processing, the greater the wounding response. Control of the wound response is the key to providing a processed product of good quality. The impact of bruising and wounding can be reduced by cooling the product before processing. Strict temperature control after processing is also critical in reducing wound-induced metabolic activity, as shown in the respiration data of intact and shredded cabbage stored at different temperatures. Other techniques that substantially reduce damage include use of sharp knives, maintenance of stringent

sanitary conditions, and efficient washing and drying (removal of surface moisture) of the cut product.

Microbiological Concerns

Fruits and vegetables are ecological niches for a diverse and changing microflora, which usually does not include types pathogenic to humans. Intact fruits and vegetables are safe to eat partly because the surface peel is an effective physical and chemical barrier to most microorganisms. In addition, if the peel is damaged, the acidity of the pulp prevents the growth of organisms, other than the acidtolerant fungi and bacteria that are the spoilage organisms usually associated with decay. On vegetables, the microflora is dominated by soil organisms. The normal spoilage flora, including the bacteria *Erwinia* and *Pseudomonas*, usually have a competitive advantage over other organisms that could potentially be harmful to humans.

Changes in the environmental conditions surrounding a product can result in significant changes in the microflora. The risk of pathogenic bacteria may increase with film packaging (high relative humidity and low oxygen conditions), with packaging of products of low salt content and high cellular pH and with storage of packaged products at too high temperatures (>5°C or 41°F). Food pathogens such as *Clostridium*, *Yersinia*, and *Listeria* can potentially develop on minimally processed fruits and vegetables under such conditions.

With minimally processed products, the increase in cutdamaged surfaces and availability of cell nutrients provides conditions that increase the numbers and types of microbes that develop. Furthermore the increased handling of the products provides greater opportunity for contamination by pathogenic organisms.

Microbial growth on minimally processed products is controlled principally by good sanitation and temperature management. Sanitation of all equipment and use of chlorinated water are standard approaches. Low temperature during and after processing generally retards microbial growth but may select for psychrotropic organisms such as Pseudomonads. Moisture increases microbial growth, therefore removal of wash and cleaning water by centrifugation or other methods is critical. Low humidity reduces bacterial growth, although it also leads to drying (wilting and shriveling) of the product. Low oxygen and elevated carbon dioxide levels, often in conjunction with carbon monoxide, retard microbial growth. Plastic film packaging materials modify the humidity and atmosphere composition surrounding processed products and therefore may modify the microbial profile.

Product Preparation

Minimal processing may occur in a "direct chain" of preparation and handling in which the product is processed, distributed, and then marketed or utilized. Many products are also handled in an "interrupted chain" in which the product may be stored before or after processing or may be processed to different degrees at different locations. Because of this variation in time and point of processing, it would be useful to be able to evaluate the quality of the raw material and predict the shelf life of the processed product.

Minimally processed products may be prepared at the source of production or at regional and local processors. Whether a product may be processed at source or locally depends on the perishability of the processed form relative to the intact form, and on the quality required for the designated use of the product. Processing has shifted from destination (local) to source processors as improvements m equipment, modified atmosphere packaging, and temperature management have become available.

In the past, processed lettuce operations often salvaged lettuce remaining in the fields after harvesting for fresh market. It is now recognized that first-cut lettuce should be used for maximum processed product quality. After trimming and coring, piece size may be reduced with rotating knives or by tearing into saladsize pieces. Damage to cells near cut surfaces influences the shelf life and quality of the product. For example, shredded lettuce cut by a sharp knife with a slicing motion has a storage life approximately twice that of lettuce cut with a chopping action. Shelf life of lettuce is less if a dull knife is used rather than a sharp knife.

Washing the cut product removes sugar and other nutrients at the cut surfaces that favor microbial growth and tissue discoloration. Because of differences in composition and release of nutrients with processing, some products such as cabbage are known as "dirty" products. It is desirable to maintain separate processing lines, or thoroughly clean the line before another product follows cabbage. Free moisture must be completely removed after washing. Centrifugation is generally used, although vibration screens and air blasts can also be used. The process should remove at least the same amount of moisture that the product retained during processing. It has been shown that removal of slightly more moisture (i.e., slight desiccation of the product) favors longer postprocessing life.

Packaging, Modified Atmospheres, and Handling

Polyvinylchloride (PVC), used primarily for overwrapping, and polypropylene (PP) and polyethylene (PE), used for bags, are the films most widely used for packaging minimally processed products. Multilayered films, often with ethylene vinyl acetate (EVA), can be manufactured with differing gas transmission rates. For lettuce processed at source, a 2.5 mil 8 percent EVA co-extruded PE bag has been used. Products are often packaged under partial vacuum or after flushing with different mixtures of gases (oxygen, carbon dioxide, carbon monoxide, and/or nitrogen). Vacuum packaging and gas flushing establish the modified atmosphere quickly and increase the shelf life and quality of processed products. For example, browning of cut lettuce occurs, before a beneficial atmosphere is established by the product's respiration. For other products, such as fastrespiring broccoli florets, impermeable barrier films are used with permeable membrane "patches" to modify the atmosphere through the product's respiration. It is not yet agreed what are the ideal films and atmospheres for minimally processed products. In addition to different atmosphere requirements for different products, the specifics of the handling chains must be taken into account, especially their time delays and temperature fluctuations.

The modified atmospheres that best maintain the quality and storage life of minimally processed products have an oxygen range of 2 to 8 percent and carbon

dioxide concentrations of 5 to 15 percent

Carbon monoxide concentrations of 5 to 10 percent under low oxygen (<5 percent) conditions retard browning and reduce microbial growth, lengthening shelf life in lettuce and other products. With some nonpermeable barrier-type PE films, an elevated oxygen level (25 to 50 percent) is used with carbon monoxide (3 to 10 percent) to maintain aerobic respiration during the handling period.

The following factors are known to be critical to maintaining quality and shelf life in minimally processed products: using the highest quality raw product, reducing mechanical damage before processing, reducing piece size by tearing or by slicing with sharp knives, rinsing cut surfaces to remove released cellular nutrients and kill microorganisms, centrifugation to the point of complete water removal or even slight desiccation, packaging under a slight vacuum with some addition of CO to retard discoloration, and maintaining product temperature at 1° to 2°C (34° to 36°F) during storage and handling. Temperature maintenance is currently recognized as the most deficient factor.

Other techniques such as irradiation, chemical preservation (dips in ascorbic acid, calcium chloride, and/or citric acid), modification of pH, and reduction of water activity (with sugars/salts) may also control deterioration of processed products, mainly by controlling microbial growth.

Quality of Minimally Processed Products

The nature of the demand for minimally processed products requires that they be visually acceptable and appealing. The products must have a fresh appearance, be of consistent quality throughout the package, and be reasonably free of defects. Field defects such as tipburn on lettuce can reduce the quality of the processed product because the brown tissue is distributed throughout the packaged product.

In mixed salads, the quality of the total product is only as good as that of the most perishable component. This also applies to cleaned and washed spinach and other products where differences in leaf age or physical damage to leaves may yield a product of nonuniform perishability.

Quality assurance programs, long regarded as essential in the processed food industry, are difficult to apply to horticultural crops and the corresponding minimally processed products. Fresh horticultural products have not yet been subjected to the same sanitation, labeling, and shelflife requirements as other processed foods.

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PACKAGING OF GROUND BEEF IN AN ATMOSPHERE WITH HIGH CARBON DIOXIDE AND LOW CARBON MONOXIDE RESTRAINS GROWTH OF *YERSINIA ENTEROCOLITICA, LISTERIA MONOCYTOGENES* AND *ESCHERICHIA COLI* O157:H7

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Abstract

Growth of the pathogens *Yersinia enterocolitica, Listeria monocytogenes, Escherichia coli* O157:H7 and strains of Salmonella was compared in ground beef packed in modified atmospheres of 60 % CO_2/ 40 % N_2 /0.4 % CO (high CO_2/ low CO mixture), 70 % O_2/ 30 % CO_2 (high O_2 mixture) and in chub packs. The ground beef was inoculated with rifampicin-resistant or nalidixic acid/streptomycin-resistant strains (final concentration 10^2-10^3 bacteria/g) and stored at 4 and 10 °C for up to 14 days. At 4 °C the shelf life based on stable colour and reduced background flora was prolonged for the high CO_2/ low CO mixture compared to the two other packaging methods, but at 10 °C the shelf life was < 8 days for all the packaging methods. Growth of *Y. enterocolitica* was nearly totally inhibited both at 4 and 10 °C in the high CO_2/ low CO mixture, while the bacterial numbers in the samples packed in the high O_2 mixture increased from about $5x10^2$ bacteria/g at day 0 to about 10^4 at day 5 at 4°C and to 10^5 at 10°C. Growth in the chub packs was even higher. *Listeria monocytogenes* showed very little growth at 4 °C in all treatments. At 10 °C there was slow growth from about $5x10^3$ bacteria/g to about 10^4 at day 5 in the high CO_2/ low CO mixture, while the numbers in the high O_2 mixture and the chub packs were about 10 times higher. Growth of *E. coli* O157:H7 at 10 °C in the ground beef was nearly totally inhibited in both the high CO_2/ low CO mixture and the high O_2 mixture. Growth in the chub packs was higher, reaching 10^5 bacteria/g on day 5. The *Salmonella* strains (*S.* Typhimurium, *S.* Dublin, *S.* Enteritidis and *S. enterica* 61:k:1,5,(7)) in the ground meat stored at 10 °C for 5 and 7 days grew to a higher number in the high CO_2/ low CO mixture than in the high O_2 mixture. This study shows that the prolonged shelf life at 4 °C did not increase growth of *Y. enterocolitica*

and *L. mononcytogenes* in ground beef stored in the high CO_2/ low CO mixture mixture, but the observed growth of strains of salmonella at 10 °C in this mixture and in chub packs does emphasise the importance of temperature control during storage.

Keywords:

Ground beef, modified atmosphere packaging, high CO_2, carbon monoxide, *Yersinia enterocolitica, Listeria monocytogenes, Escherichia coli* O157:H7.

1. Introduction

Ground beef for retail sale is most often ready-packed in modified atmospheres (MA) or in chub packs. MA-packed ground beef has a longer microbiological shelf life and also maintains an attractive red colour. For the past decade the Norwegian meat industry has been using a gas mixture of 60-70 % CO_2, 30-40 % N_2, 0.3-0.5 % CO. (The CO comes ready mixed in the N_2 from the supplier.) The reason for adding CO to the gas mixture is that it will produce a long-lasting cherry-red colour of the meat (Sørheim et al., 1999), but the low concentration of CO has little effect on the microflora of the meat (Clark et al., 1976; Gee and Brown, 1978; Luno et al., 1998). The use of CO at such low concentrations does not present any toxic threat to the consumers (Sørheim et al., 1997). The most commonly used gas mixture for retail-ready meat in other European countries is 70 % O_2/30 % CO_2 (Gill, 1996). The high oxygen concentration is needed to keep the red colour of the meat (Lambert et al., 1991). It is therefore only possible to obtain half the CO_2 concentration used in the high CO_2/ low CO mixture. The microbiological shelf life of the high O_2 mixture will be longer than in air, but less than in the high CO_2/ low CO gas mixture (Sørheim et al., 1999).

The inclusion of CO is controversial because the stable cherry–red colour can last beyond the microbiological shelf life of the meat and thus mask spoilage (Kropf, 1980). The extended shelf life obtained by MAP may under some conditions imply increased risk of growth of pathogens (Silliker and Wolfe, 1980; Hintlian and Hotchkiss, 1986; Farber, 1991; Lamberts et al., 1991). This issue has also been discussed by the European Commission (1997).

However, even if meat packed in high CO_2/ low CO mixture acquires a stable colour, the shelf life based on odour is significantly longer in the high CO_2/ low CO

mixture only at 4 °C (Sørheim et al., 1999). At this temperature *Yersinia enterocolitica* and *Listeria monocytogenes* are considered to be the most serious pathogens in meat. At abuse temperatures (>8 °C) *Escherichia coli* O157:H7 and *Salmonella* spp. also may grow and increase the health risk to the consumers. In the present study we wanted to compare growth of these pathogens in ground beef packed in a commercial Norwegian 60 % CO_2/40 % N_2./0.4 % CO (high CO_2/low CO mixture) with growth in a high O_2 (70 % O_2/30 % CO_2) gas mixture and in ground beef in chub packs during storage at 4 and 10 °C in order to evaluate the microbiological safety of the product.

2. Materials and methods

2.1. Preparation and packaging of the ground beef

The beef carcasses were de-boned, and trimmings with 14 % fat were ground through a 4 mm plate. The batch of ground beef was divided into 500 g portions which were packaged in 0.4 % CO/ 60 % CO_2/ 40 % N_2 (high CO_2/ low CO mixture), 70 % O_2/ 30 % CO_2 (high O_2) or packed in clipped chub packs. The beef was packed at a commercial meat plant within 1 hour of grinding as described by Sørheim et al. (1999).

2.2. Bacterial cultures and growth conditions

Strains of the following pathogens were inoculated in the ground beef: *Yersinia enterocolitica* (mixture of 3 strains), *Listeria monocytogenes* (mixture of 3 strains isolated from cooked sausage, Blom et al., 1997, Nissen and Holck, 1999), *Escherichia coli* O157:H7, NCTC 1200 (National Collection of Type Cultures,

Colindale, London), non-toxic strain (resistant to 100 µg/ml nalidixic acid and 1000 µg/ml streptomycin) and *Salmonella enterica* subspecies *diarizonae* serovar 61:k:1,5,(7) (*S. enterica* 61:k:1,5,(7)), mixture of 3 strains (National Institute of Public Health, Oslo). The listeria and yersinia strains were made resistant to rifampicin by spreading 0.1 ml of overnight cultures onto agar plates of TSB medium (Oxoid, CM 129) containing 50 µg/ml rifampicin (Sigma, St.Louis, MO, USA). The growth rates of the resistant strains were practically equal to those of the parent strains when tested in TSB medium in a Bioscreen instrument (Labsystem Co., Helsinki, Finland) at the same temperature, pH and a_w (NaCl) concentrations.

In a second experiment four rifampicin-resistant salmonella strains, *S.* Typhimurium, *S.* Dublin, *S.* Enteritidis and *S. enterica* 61:k:1,5,(7) were used to inoculate the MAP- packed ground beef. The growth rates (measured as above) of the resistant strains of *S.* Enteritidis and *S. enterica* 61:k:1,5,(7) were essentially the same as the parent strains while the growth rates of *S.* Dublin and *S.* Typhimurium were slightly lower.

2.3. Inoculation and storage

After packaging the ground beef was inoculated with stationary cultures (the bacteria were cultivated overnight at 30°C and kept in the refrigerator for 1 day before use) of the different pathogenic bacteria. The stock cultures were diluted in peptone water (PW) (Bacto peptone, Difco, 1g/l; NaCl, Merck, 8.5 g/l) and the strains belonging to the same species or serovars were mixed. Fifty µl of each pathogen were inoculated with a syringe through a gas probe self-sealing tape (Toray Engineering Co. Ltd, England) into one of the corners of the MA packages. The packages thus had one pathogen inoculated in each corner. In the chub packs the

pathogens were inoculated at least 3 cm apart. Packages inoculated only with *Y. enterocolitica* and *L. monocytogenes* only were stored at 4°C and analysed after 0, 2, 5, 8 and 14 days while packages inoculated with all 4 pathogens were stored at 10 °C and analysed after 0, 2, 5 and 8 days.

In the second experiment four serovars of «*Salmonella*» were inoculated in one corner each of the package of ground beef and which was stored at 10 °C and analysed after 0, 2, 5 and 7 days. Non-inoculated packages used as controls were also stored at 10 °C.

2.4. Microbial analyses

Samples of 25 g ground beef containing the inoculated pathogens were transferred to a stomacher bag and mixed with 150 ml peptone water (8.5 g NaCl, 1.0 g peptone/1000 ml water). One hundred µl of a ten-fold dilution series were plated on blood agar containing 50 µg/ml rifampicin for *L. monocytogenes* and *Y. enterocolitica* or 100 µg/ml nalidixic acid and 1000 µg/ml streptomycin sulphate for *E. coli* O157:H7. From the undiluted mixture an aliquot of 1 ml was also plated out. For enumeration of *Salmonella* spp. the selective medium Brilliant Green Agar (modified) (BGA; Oxoid, Basingstoke, Hampshire, England) was used. The colonies were confirmed on Triple Sugar Iron Agar (TSI; Difco, Detroit, MI,) and Urea agar (Urea Agar Base, Oxoid CM53 and Urea Solution, Oxoid SR20) followed by agglutination by monovalent antisera (provided by the National Institute of Public Health). In the second experiment, samples for detection of the four salmonella strains were plated on blood agar containing 50 µg/ml rifampicin samples from non-inoculated packages were treated the same way and plated on MRS plates (CM359, Oxoid), pH 5.7, for determination of lactic acid bacteria and PCA (Difco, Detroit, MI, USA) plates for total

counts of bacteria. The plates were incubated at 30°C for up to 2 days, all aerobically. On each sampling date the packs with MA were analysed for O_2 and CO_2 and the pH for all samples was measured in the stomacher solution. Samples from two replicate packages were used for all analyses, except after 7 days storage in experiment 2 where three replicate packages were analysed.

2.5. Statistical analyses

Microbial data were subjected to analysis of variance (ANOVA) and Tukey's pairvise comparisons. It was deemed appropriate to perform ANOVA on these data after a $\log_{10}$ transformation, thereby obtaining a distribution more akin to the normal distribution on which ANOVA is based.

3. Results

As expected the shelf life of the ground beef stored at 4 °C was prolonged in the high CO_2/ low CO mixture compared with the other packaging methods. This was due to the stable colour and reduced background flora resulting in little off-odour. Thus the ground beef packed in the high CO_2/ low CO mixture still had an acceptable smell after 14 days of storage at 4 °C, while the beef packed in high O_2 mixture and in the chub packs had some off-odours. The difference in shelf life was less at 10 °C. After 5 days storage the ground beef packed in the high CO_2/ low CO mixture had an acceptable smell (except the packages inoculated with salmonella, while beef packed in the high O_2 mixture and the chub packs had a slight off-odour.

After 8 days storage there was a strong off-odour for all treatments, but the ground beef in the high CO_2/ low CO mixture still looked bright red, in accordance with Sørheim et al. (1999). The O_2 content in the high CO_2/ low CO mixture was virtually

zero throughout storage at both temperatures. At 10 °C the O_2 content in the high O_2 gas mixture decreased from 70 to about 35 % after 8 days storage, probably due to aerobic bacterial metabolism. The chub packs had an O_2-permeable casing which probably was the cause of the high bacterial growth in these packs at both temperatures.

Growth of *Y. enterocolitica* was totally inhibited both at 4 and 10 °C in the high CO_2/ low CO mixture (Fig. 1a and b), while the number in the samples packed in the high O_2 mixture increased from about $5x10^2$ cfu/g at day 0 to about 10^4 cfu/g at day 5 at 4 °C and to 10^5 cfu/g at 10°C. Growth in the chub packs at 4 °C was even higher than in the other treatments. Growth in chub packs was also higher than in high O_2 at 10 °C p=0.007). *L. monocytogens* (Fig. 2a) showed very little growth at 4 °C in all treatments. At 10 °C (Fig. 2b) there was slow growth (from about $5x10^3$ bacteria/g to about 10^4 at day 5) in the high CO_2/ low CO mixture. This was more than 10-fold higher cfu/g at day 5 than in the high O_2 mixture (p= 0.040) and the chub packs (p=0.035). Ground beef inoculated with *E. coli* O157:H7 and strains of salmonella was stored at 10°C. Growth of *E. coli* O157:H7 was slow both in the high CO_2/ low CO mixture and the high O_2 mixture (Fig. 3) and the numbers were less than 10^4 cfu/g at day 5. Growth in the chub packs was greater than in the high CO_2/ low CO-mixture (p=0.011) and in the high O_2 mixture (p=0.019), reaching 10^5 cfu/g. Growth of lactic acid bacteria in the non-inoculated packages was somewhat inhibited in the high CO_2/ low CO mixture, especially at 4 °C (Fig. 4). At start of the experiment the pH in the ground beef was about 5.8 in all packages. After 5 days storage the pH was about 5.7 in the high CO_2/ low CO mixture, 5.5 in the high O_2 mixture and 5.3 in the chub packs.

Due to growth of other bacteria on the selective plates, only approximate numbers of *S. enterica* 61:k:1,5,(7) were obtained, but growth of about 1.5 log units was observed both in the CO mixture and the chub packs (results not shown). This increase was not seen in the high O_2 mixture. To verify these results and check whether they were valid for other serovars more virulent to humans, such as *S.* Typhimurium, *S.* Dublin and *S.* Enteritidis, a second experiment was performed. The results (Fig. 5 a, b, c and d) show that after 2 days of storage at 10 °C there was essentially no growth of the salmonella strains in ground beef packed in the high CO_2/ low CO mixture and in the high O_2 mixture, while the numbers of salmonella in the chub packs were about 10 fold higher. After 5 days there was a slight off-odour in all the packages except for one package with high CO_2/ low CO mixture which smelled strongly of H_2S. In this package the numbers of all the salmonella strains were higher than in the replicate package and were of the same magnitude as the numbers in the chub packs. In the O_2 mixture there was no growth of *S.* Dublin and *S.* Enteritidis and only a low growth of *S. enterica* 61:k:1,5,(7) and *S.* Typhimurium. The growth of the salmonella strains was still greatly inhibited in the high O_2 mixture, while growth in the high CO_2/ low CO mixture was just as high or even higher than in the chub packs.

In the non-inoculated packages the lactic acid bacteria rapidly constituted most of the background flora (not shown). After 5 days storage the numbers were higher in the chub-packed samples, but after 8 days there were no obvious differences (Fig. 6). The pH in the non-inoculated ground beef followed the same pattern as in experiment 1.

4. Discussion and Conclusions

Ground beef is a high-risk product because pathogens may be mixed into the ground product which may not be sufficiently heated before consumption. To inhibit growth of spoilage bacteria and increase shelf life, MAP is often used by retailers. The question «Do modified atmospheres enhance risk to the consumers health, but delay signs of spoilage» raised by Hintlian and Hotchkiss (1986) is therefore relevant. When evaluating the safety of ground beef in the high CO_2/ low CO mixture compared to other commercially available packaging methods, we have focused on bacteria that show good growth below 10 °C and are most relevant for meat products.

The ability of *Y. enterocolitica* to multiply at low temperature is of considerable concern to food producers, particularly in countries like Australia, Canada, Denmark, Germany, New Zealand, Norway and Sweden where *Y. enterocolitica* has surpassed *Shigella* and now rivals *Salmonella* and *Campylobacter* as a cause of acute bacterial gastroenteritis (Nesbakken, 1999). In our study, growth of *Yersinia enterocolitica* was totally inhibited in ground beef packed in the high CO_2/ low CO mixture even at 10 °C while it grew fairly well both in the high O_2 mixture and in the chub packs. Manui-Tawiah et al. (1993) found that pork shops packed in different MA with 20 or 40 % CO_2 with or without O_2 allowed growth of *Yersinia enterocolitica*, but here the CO_2 concentration was lower than in the high CO_2/ low CO mixture (60 %) used in our study.

Listeria monocytogenes is also a pathogen that grows well at low temperatures, but in our study there was no growth of this bacterium in the ground beef in any of the packages at 4 °C, and only slow growth at 10 °C. This agrees with results of

Farber and Daley (1994) who found no growth of *L. monocytogenes* in different meat products when stored at 4 °C.

At the abusive storage temperature of 10 °C, *E. coli* O157:H7 in the chub packs grew about as fast as the background flora. However, growth was nearly totally inhibited in the high CO_2/ low CO mixture and in the high O_2 mixture. This is in accordance with the predictive model of Sutherland et al. (1997). Their study showed that *E. coli* O157:H7 is relatively tolerant of CO_2, but growth could be inhibited at 10 °C at high CO_2 concentrations and pH < 6.0.

In our study, growth of *Salmonella* spp. was not inhibited in ground beef packed in high CO_2/ low CO mixture and stored at 10 °C, contrary to what is found in many other studies (e.g. D'Aoust, 1991). Although salmonella may grow well and out-compete the background flora on fresh meat stored at 10 °C (Alford and Palumbo, 1969; Mackey and Kerridge, 1988), most reports claim that growth will be inhibited in MAP at this temperature (Siliker and Wolfe, 1980; D'Aoust, 1991; Gill and DeLacy, 1991). Nychas and Tasson (1996) found that high CO_2 atmospheres were more inhibitory for growth of *S.* Enteritidis on fresh poultry at 10 °C than were high O_2 atmospheres, the opposite of what we found for ground beef. Inhibition of bacterial growth may, however, be influenced by pH, texture and the composition of the product, and Gill and DeLacy (1991) did find growth of *S.* Typhimurium in high-pH beef packed in CO_2 and stored at 10 °C. Oxidative stress reactions in salmonella have recently been reported (Stephen et al., 1999). This may explain the inhibition of growth (longer lag phase) in the high O_2 mixture in our study.

The present study shows that the prolonged shelf life (due to stable colour and reduced background flora) at 4 °C did not increase the risk of growth of *Y. enterocolitica* and *L. monocytogenes* in ground beef stored in the high CO_2/ low CO

gas mixture. This is probably due to the high CO_2 concentration that is inhibitory to most microorganisms (Dixon and Kell, 1989). Even at the abusive temperature of 10 °C, the numbers of pathogens at the end of the shelf life (5 days) were less or the same as were found in the chub packs. The observed growth of salmonella in the CO mixture and chub packs does however emphasise the importance of temperature control during storage. There is a wide range of temperature criteria for chilled foods at retail in European countries. The values range from –1 °C to 10 °C, with most temperatures being between 4 and 8 °C (European Commission, 1996). These aspects should also be considered together with the conclusions of the EU report (European Commission, 1997) which state that MAP has proven to enhance the product quality by inhibiting the spoilage bacteria. MAP may also constitute a hurdle to the growth of some pathogens, and the safety of MAP products are mostly threatened by temperature abuse.

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Fig. 1. Growth of *Yersinia enterocolitica* inoculated in ground beef packed in high CO_2/ low CO mixture (0.4 % CO/ 60 % CO_2/ 40 % N_2), high O_2 (70 % O_2/ 30 % CO_2) or in chub packs. The ground beef was stored at **a**, 4 °C or **b**, 10 °C.

Fig. 2. Growth of *Listeria monocytogenes* inoculated in ground beef packed in high CO_2/ low CO mixture (0.4 % CO/ 60 % CO_2/ 40 % N_2), high O_2 (70 % O_2/ 30 % CO_2) or in chub packs. The ground beef was stored at **a**, 4 °C or **b**, 10 °C.

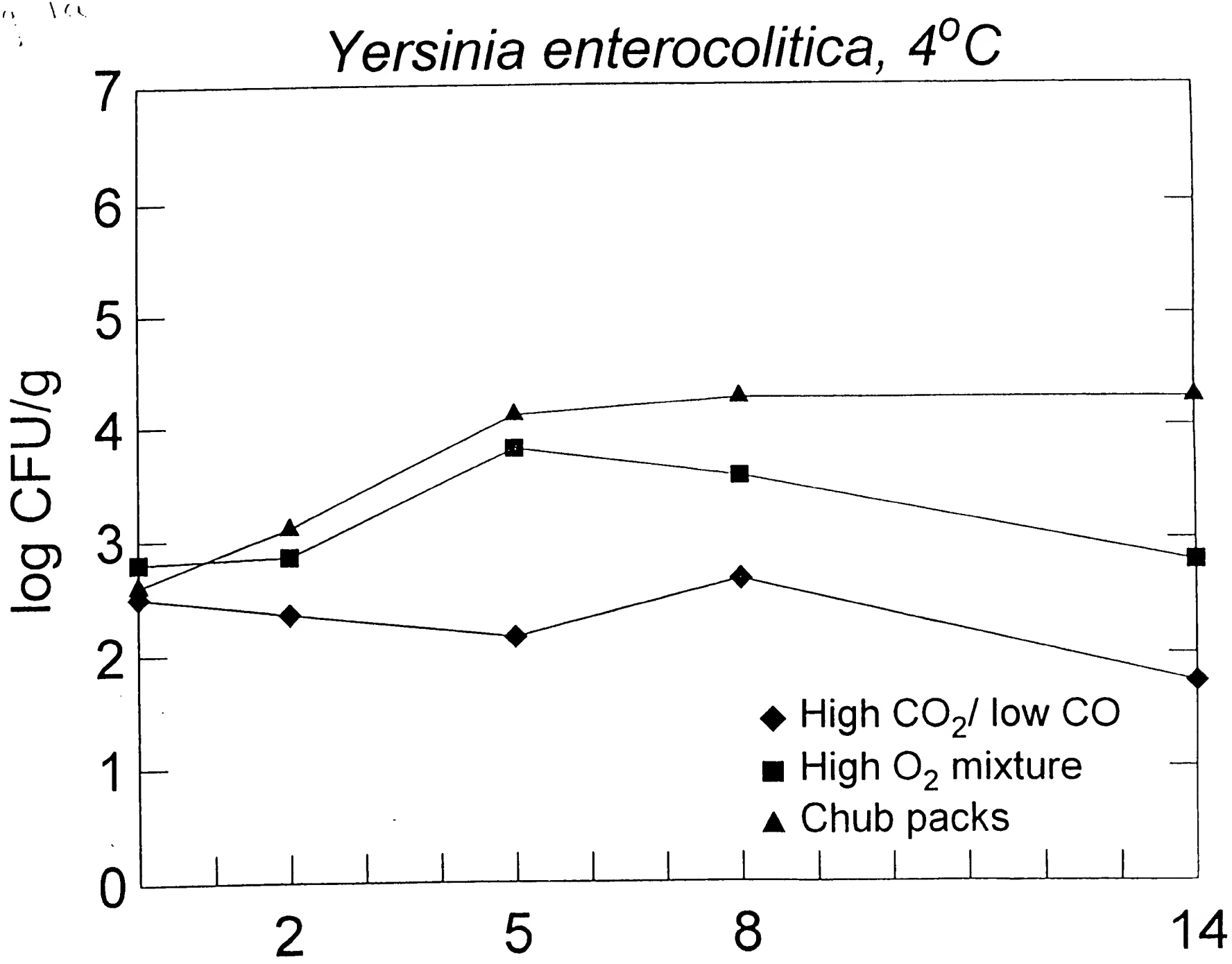
Fig. 3. Growth of *Escherichia coli* O157: H7 inoculated in ground beef packed in high CO_2/ low CO mixture (0.4 % CO/ 60 % CO_2/ 40 % N_2), high O_2 (70 % O_2/ 30 % CO_2) or in chub packs, stored at 10 °C.

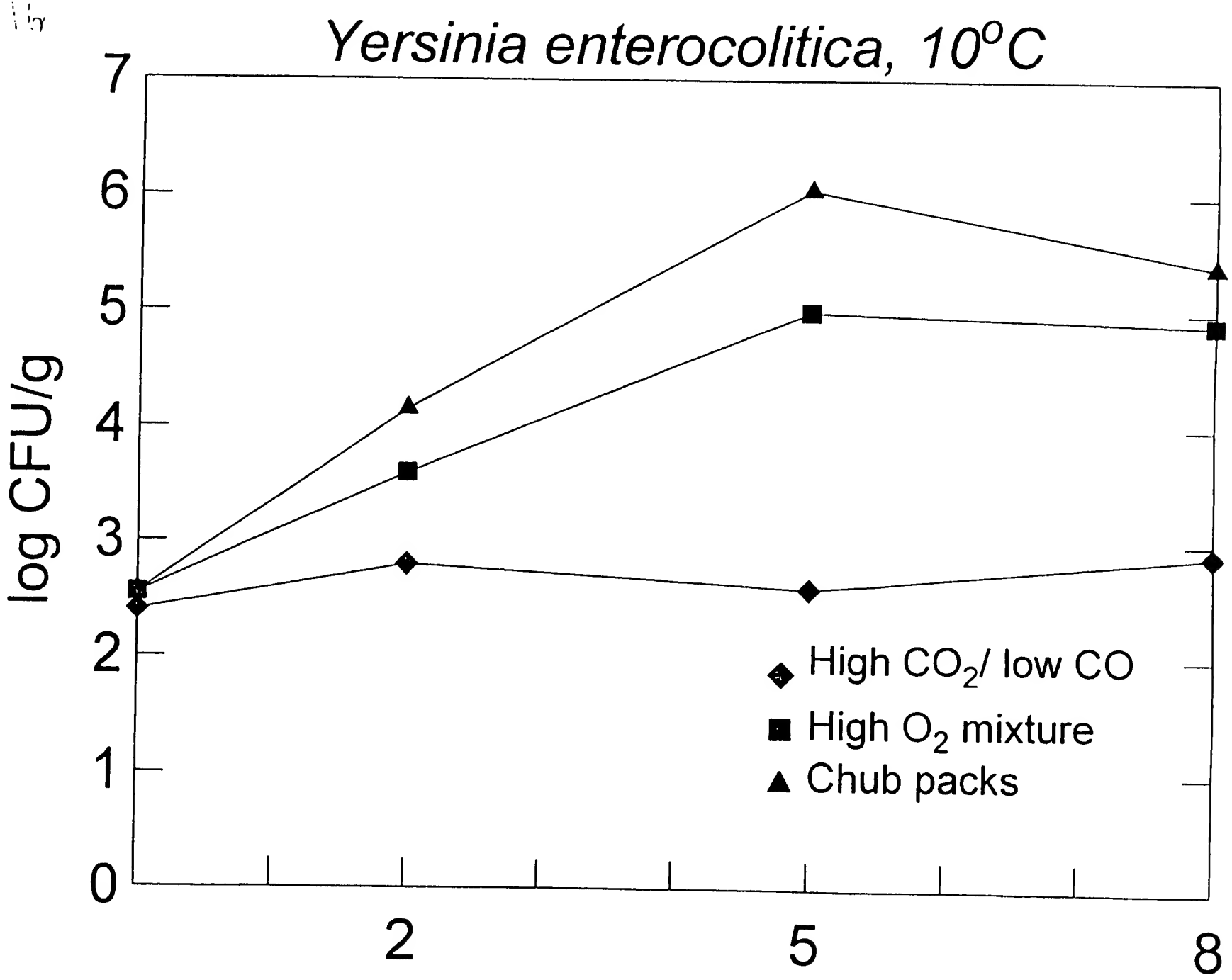
Fig. 4. Growth of lactic acid bacteria (cfu/g on MRS, pH 5.7) in non-inoculated ground beef packed in high CO_2/ low CO mixture (0.4 % CO/ 60 % CO_2/ 40 % N_2), high O_2 (70 % O_2/ 30 % CO_2) or in chub packs. The ground beef was stored at **a**, 4°C or **b**, 10 °C.

Fig. 5. Growth of strains of *Salmonellae* inoculated in ground beef packed in high CO_2/ low CO mixture (0.4 % CO/ 60 % CO_2/ 40 % N_2), high O_2 (70 % O_2/ 30 % CO_2) or in chub packs, stored 10 °C. **a.** *S.*Typhimurium **b.** *S.* Dublin **c.** *S.* Enteritidis **d.** *S. enterica* 61:k:1,5,(7).

Fig. 6. Growth of lactic acid bacteria (cfu/g on MRS, pH 5.7) in non-inoculated ground beef packed in high CO_2/ low CO mixture (0.4 % CO/ 60 % CO_2/ 40 % N_2), high O_2

(70 % O_2/ 30 % CO_2) or in chub packs. The ground beef was stored at **a**, 4 °C or **b**, 10 °C.


Yersinia enterocolitica, 4°C
log CFU/g
0
1
2
3
4
5
6
7
2
5
8
14
High CO2/ low CO
High O2 mixture
Chub packs


Yersinia enterocolitica, 10°C
log CFU/g
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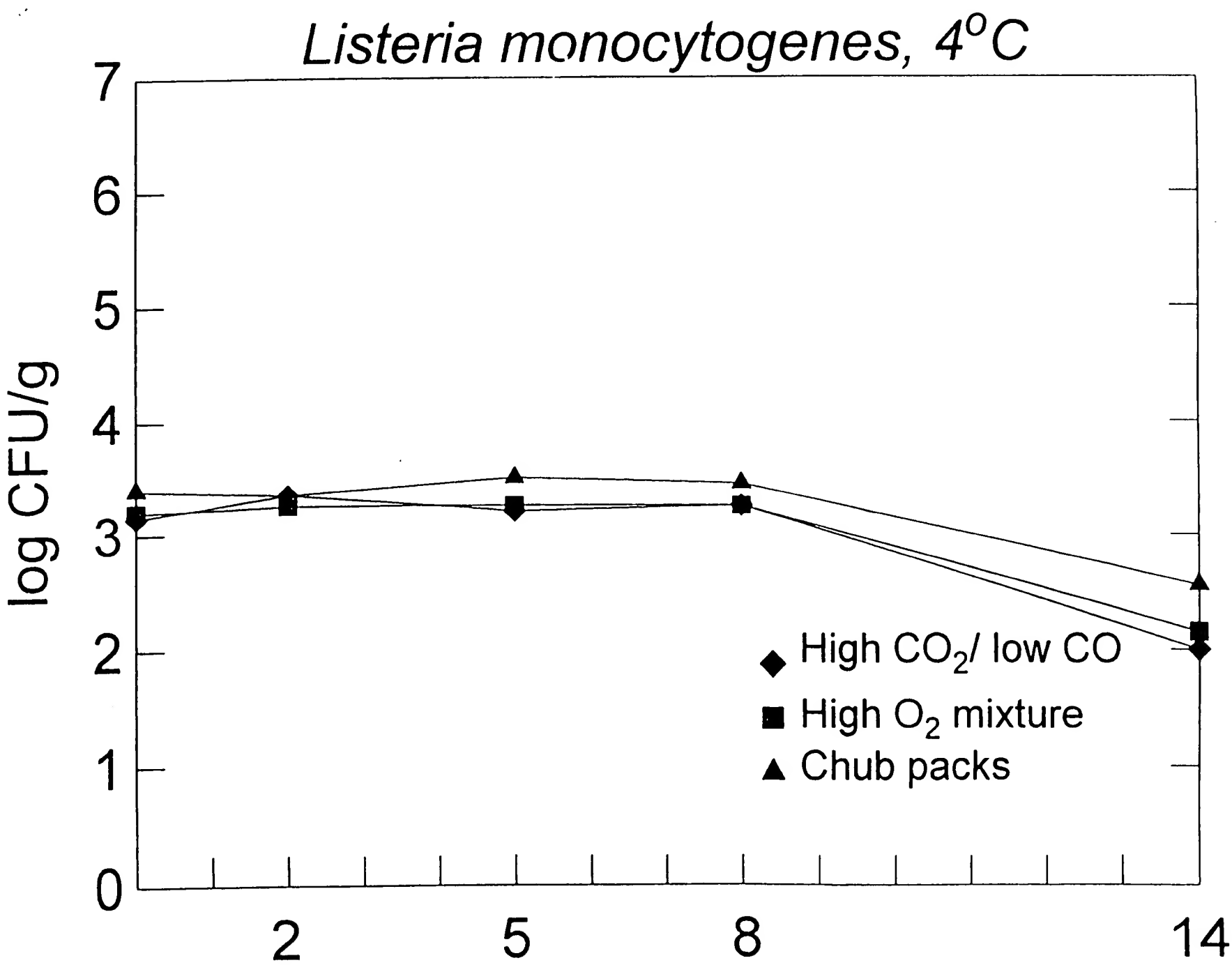
6
5
4
3
2
1
0
2
5
8
High CO2/ low CO
High O2 mixture
Chub packs


Listeria monocytogenes, 4°C
log CFU/g
0
1
2
3
4
5
6
7
2
5
8
14
High CO2/ low CO
High O2 mixture
Chub packs

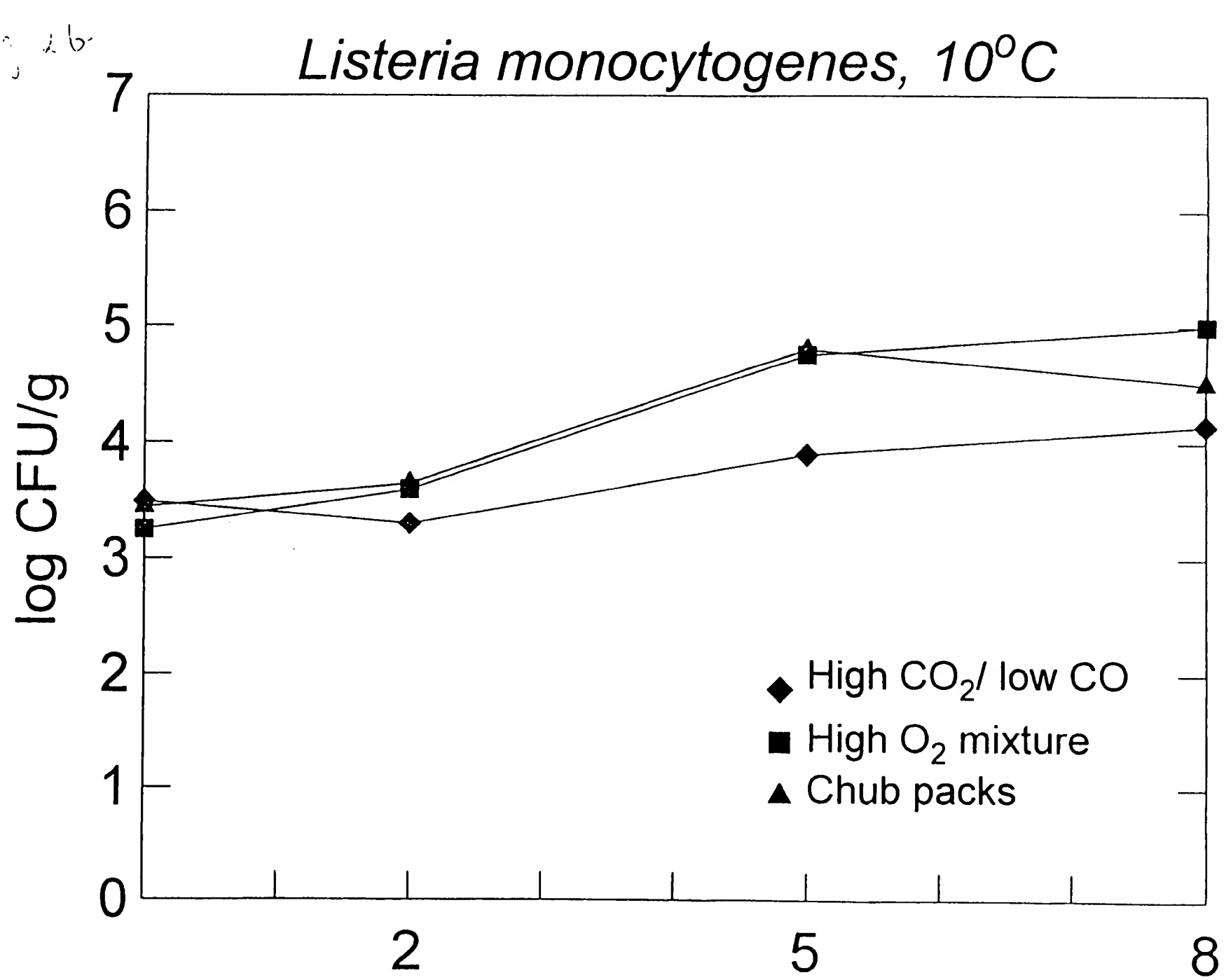
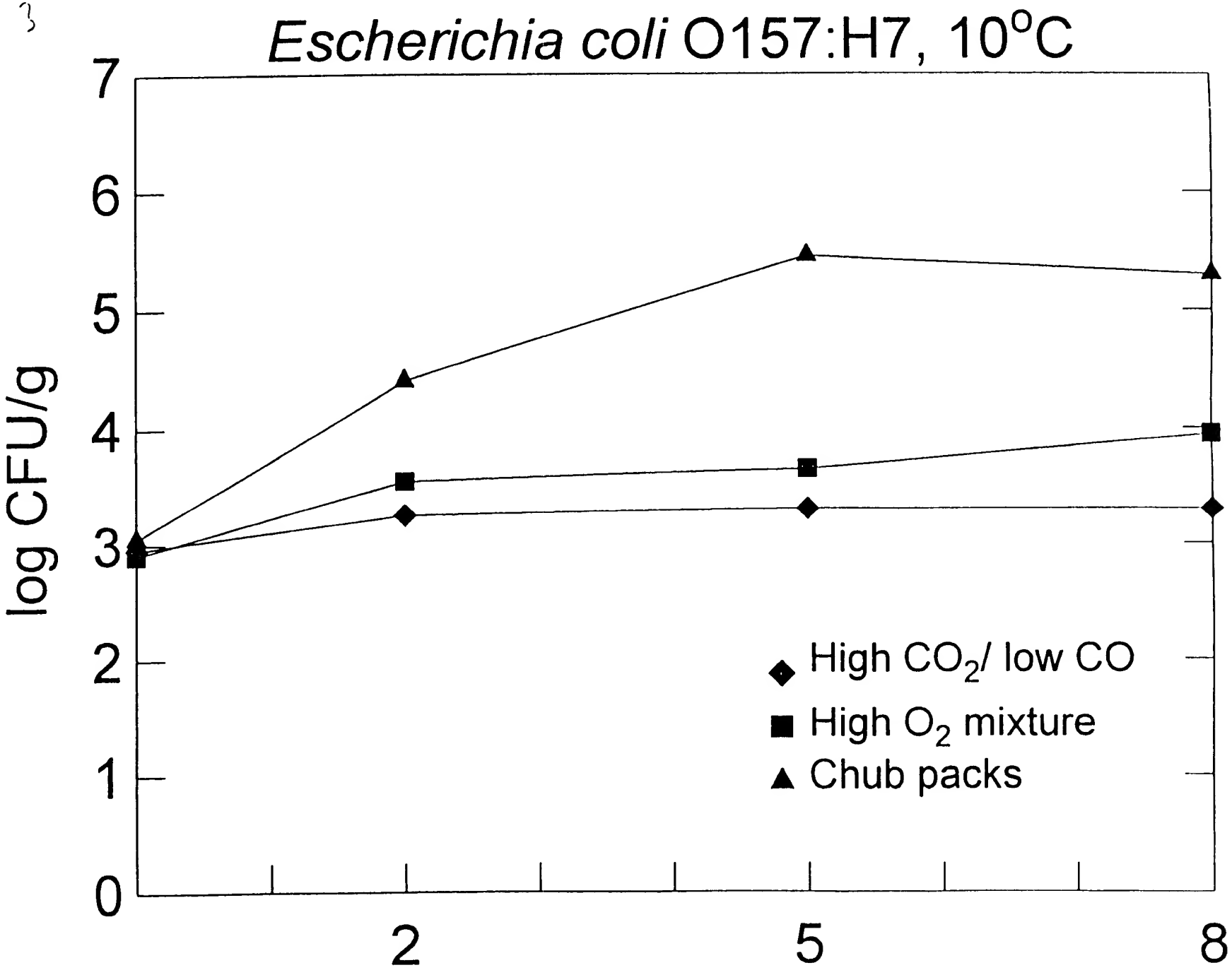

Listeria monocytogenes, 10°C
log CFU/g
0
1
2
3
4
5
6
7
2
5
8
High CO2/ low CO
High O2 mixture
Chub packs

Fig 3


Escherichia coli O157:H7, 10°C
log CFU/g
0
1
2
3
4
5
6
7
2
5
8
High CO2/ low CO
High O2 mixture
Chub packs

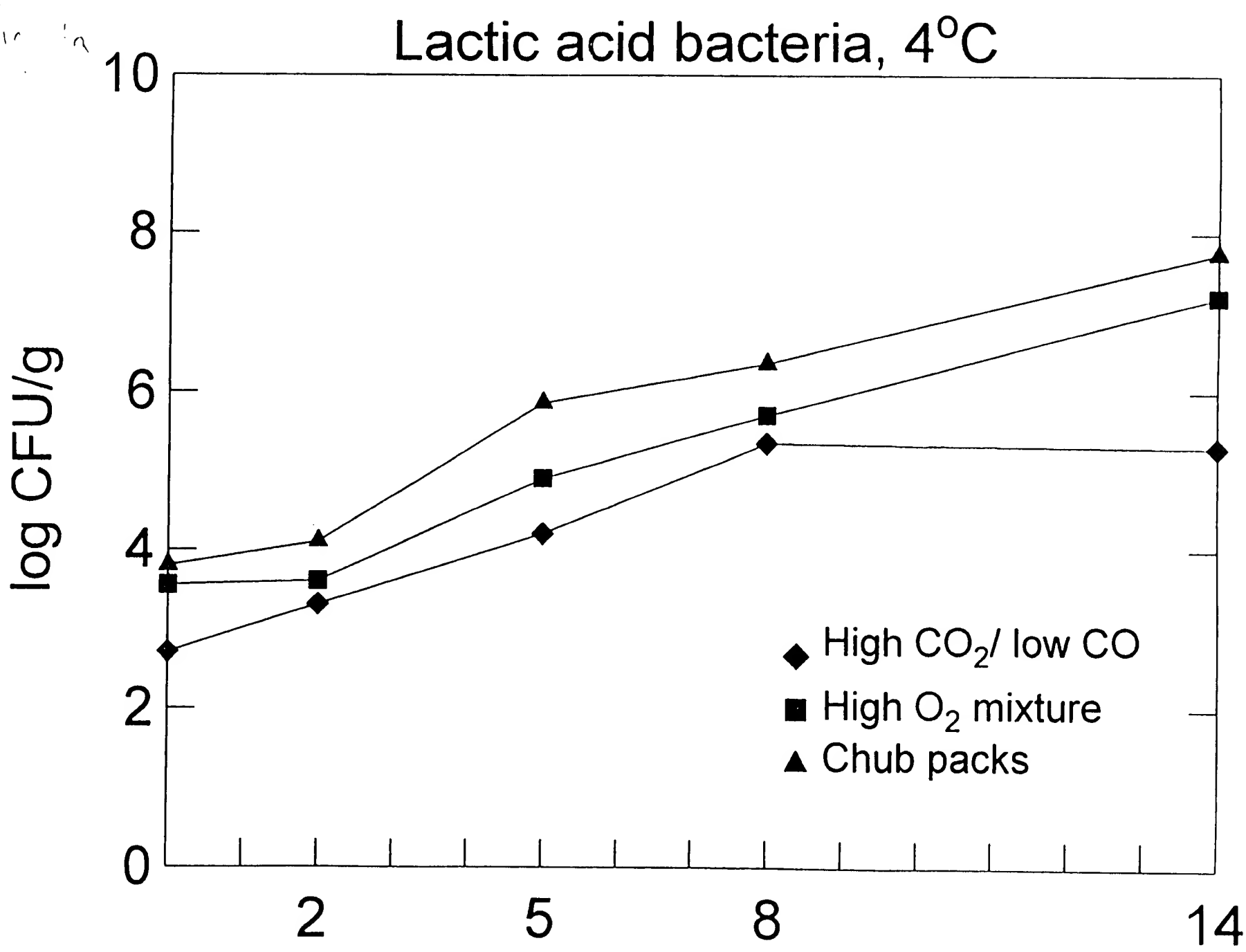

Lactic acid bacteria, 4°C
log CFU/g
10
8
6
4
2
0
2
5
8
14
High CO_2/ low CO
High O_2 mixture
Chub packs

Fig. 4b

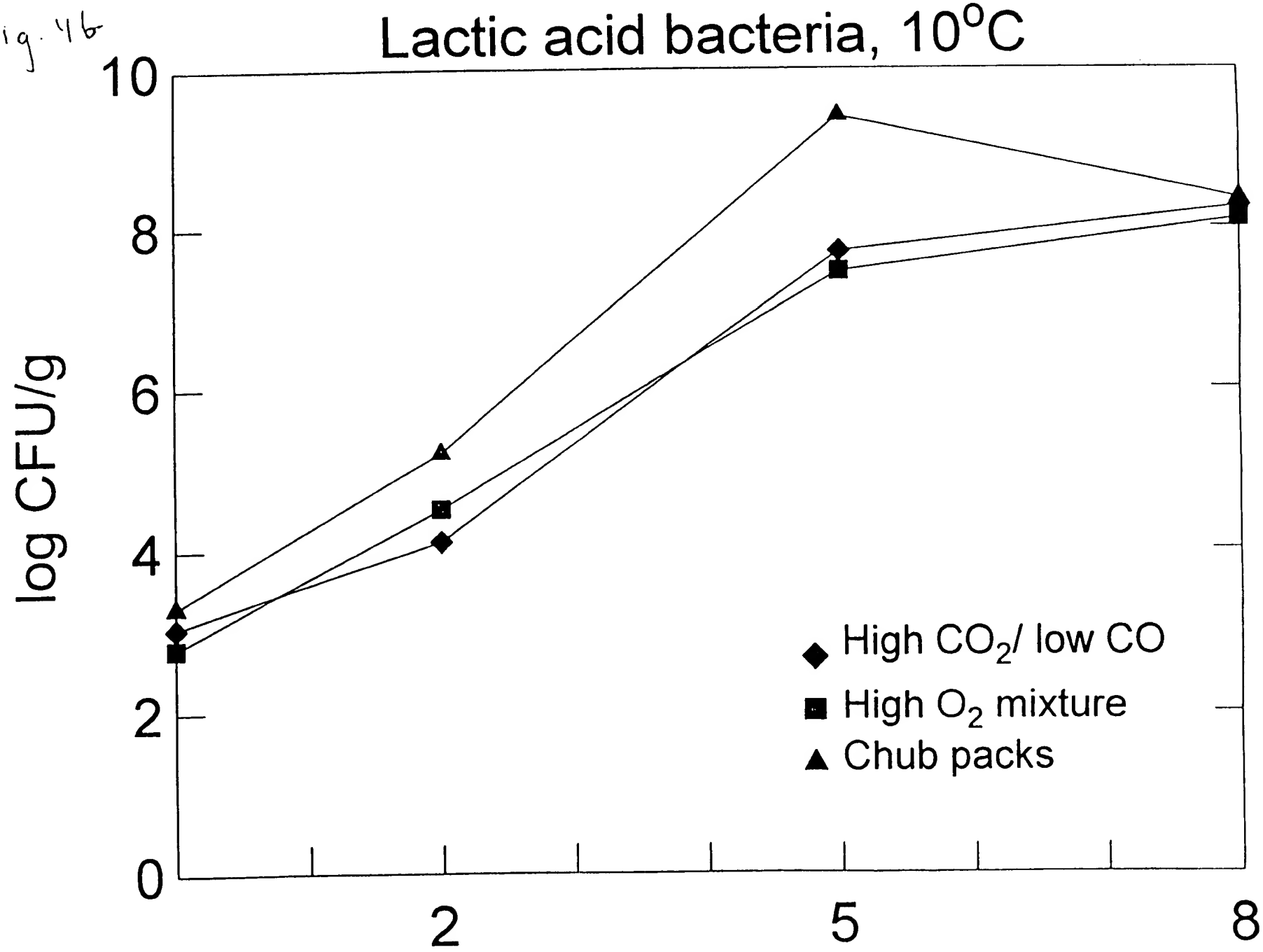

Lactic acid bacteria, 10°C
log CFU/g
10
8
6
4
2
0
2
5
8
High CO_2/ low CO
High O_2 mixture
Chub packs

Fig. 5a

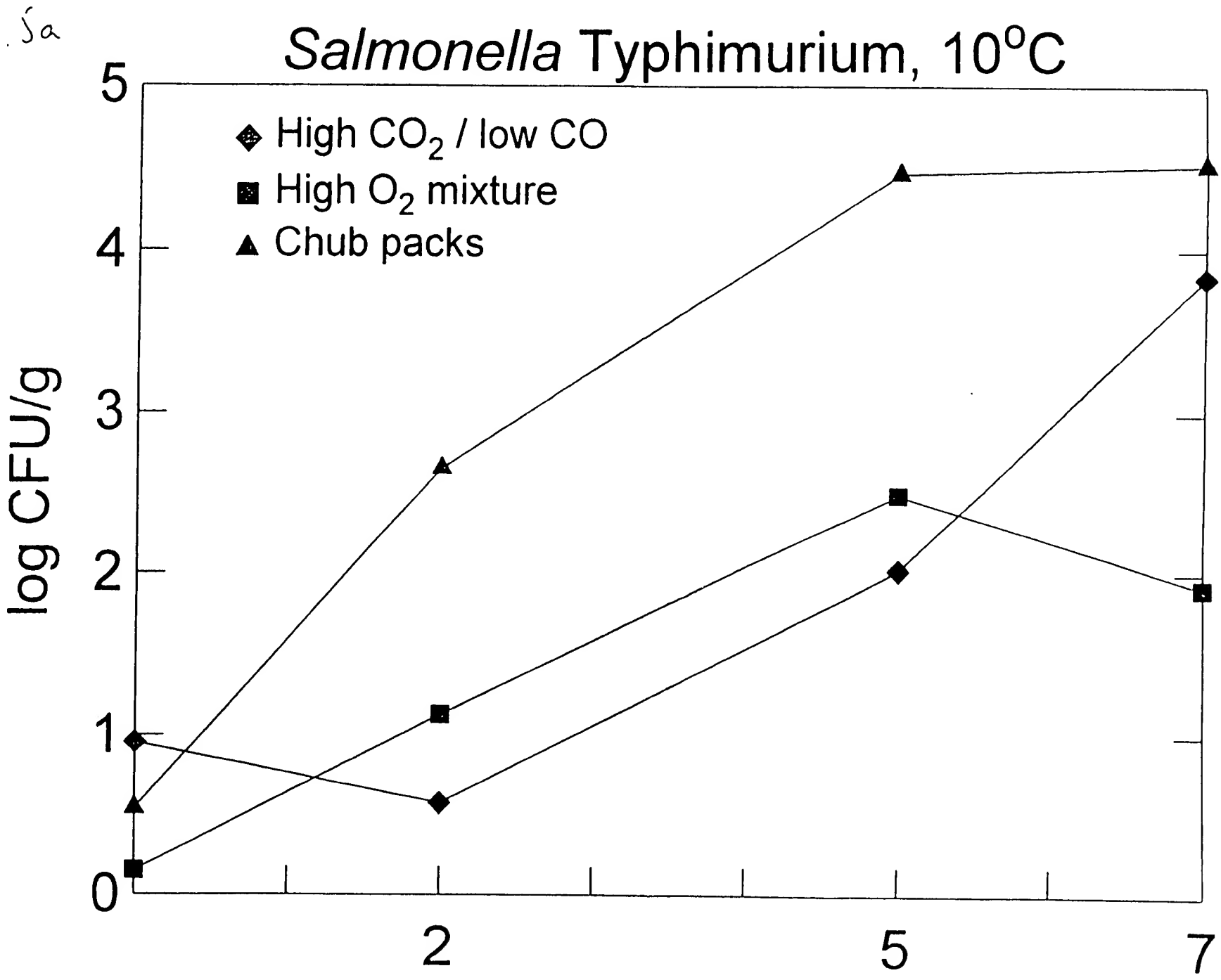
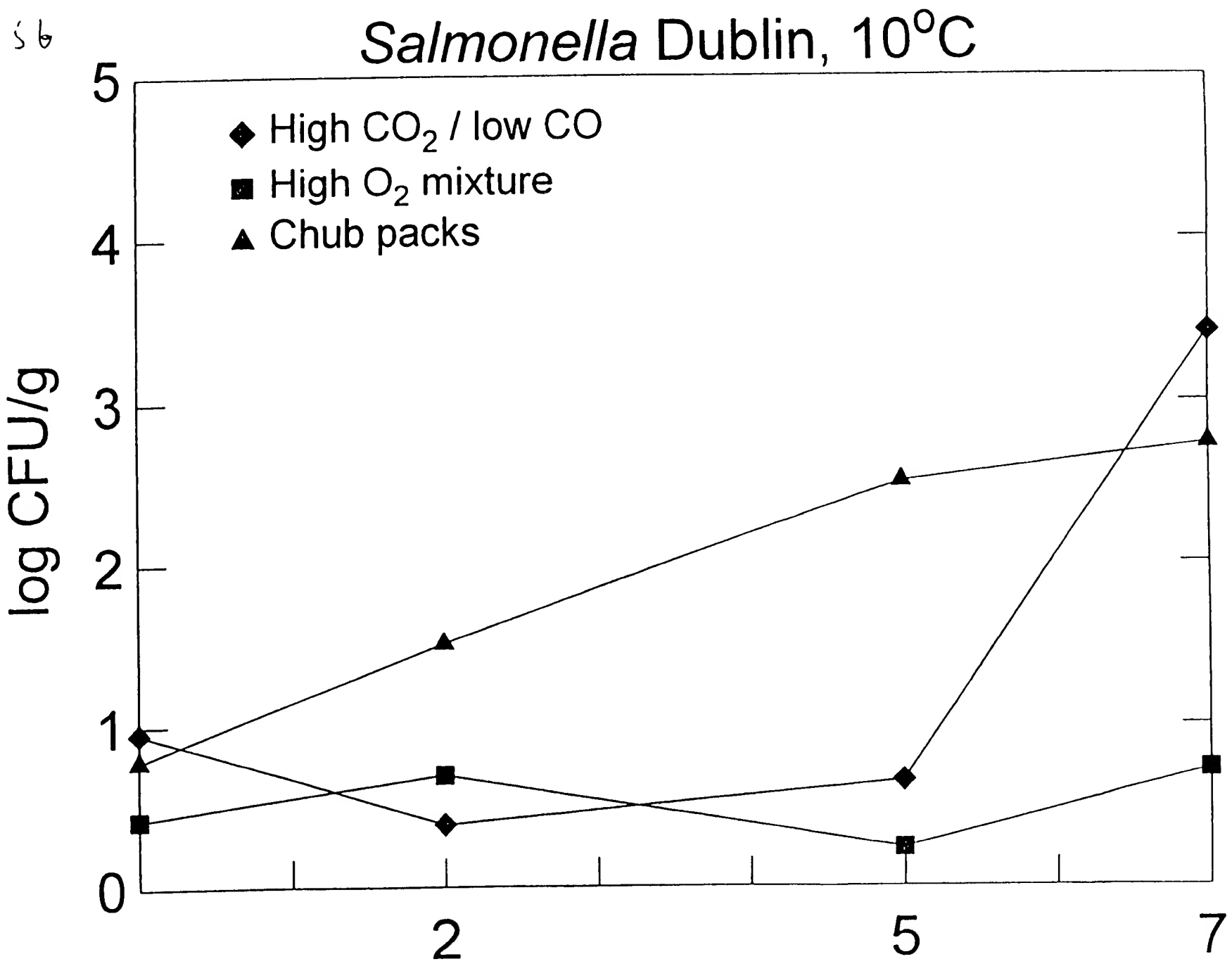

Salmonella Typhimurium, 10°C
High CO2 / low CO
High O2 mixture
Chub packs
log CFU/g
0
1
2
3
4
5
2
5
7

Fig 5b


Salmonella Dublin, 10°C
High CO_2 / low CO
High O_2 mixture
Chub packs
log CFU/g
0
1
2
3
4
5
2
5
7

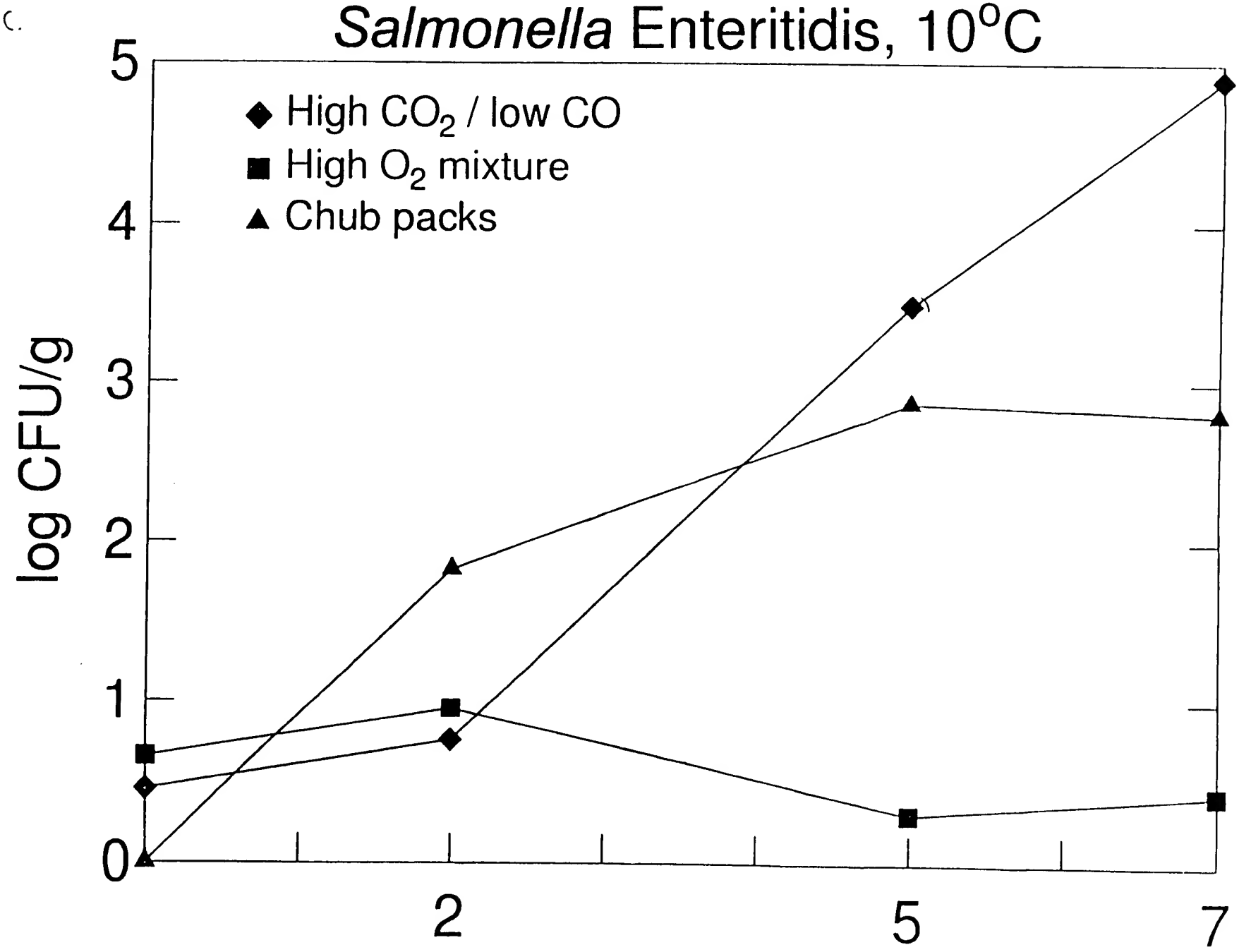

Salmonella Enteritidis, 10°C
High CO_2 / low CO
High O_2 mixture
Chub packs
log CFU/g
0
1
2
3
4
5
2
5
7

Fig. 5d

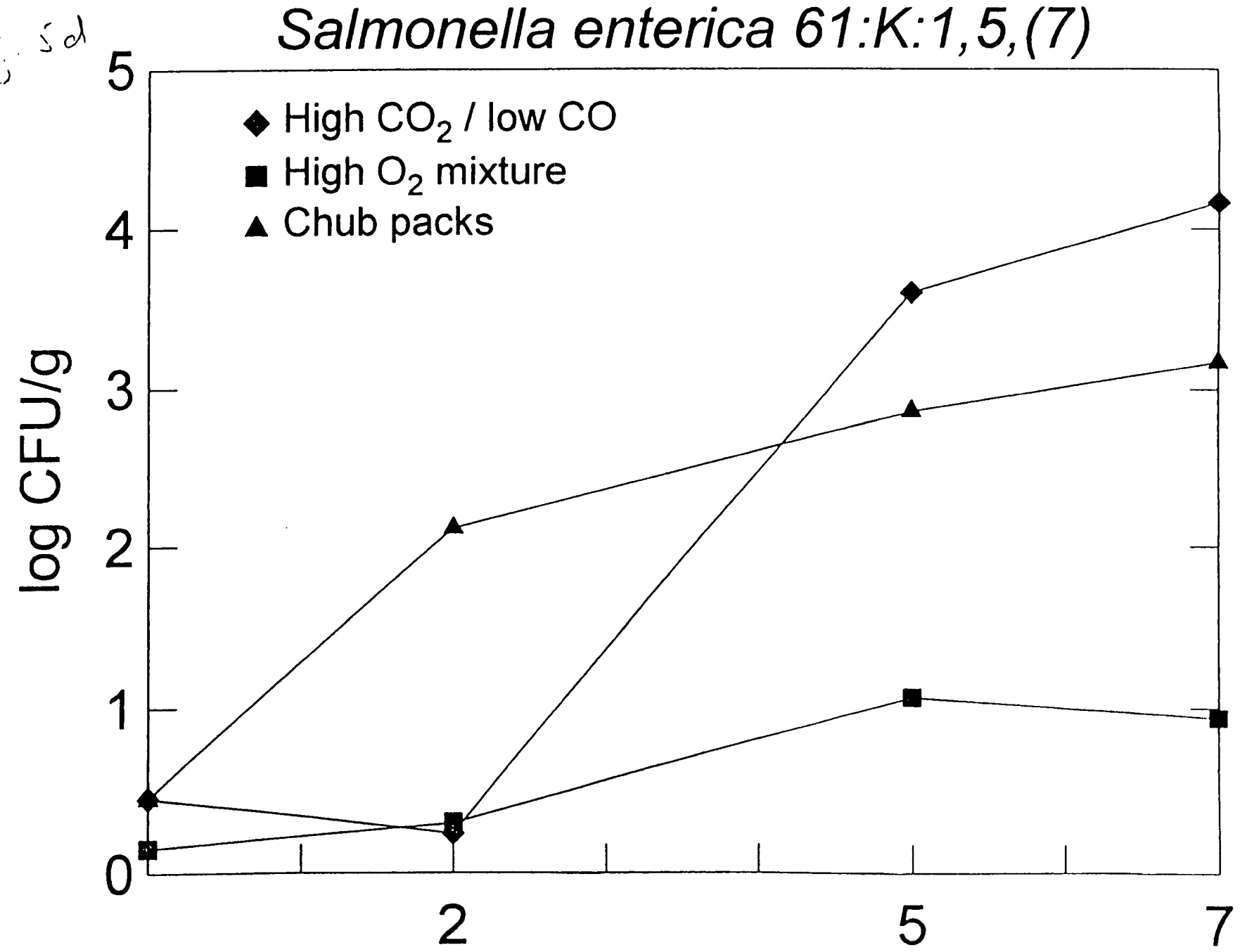
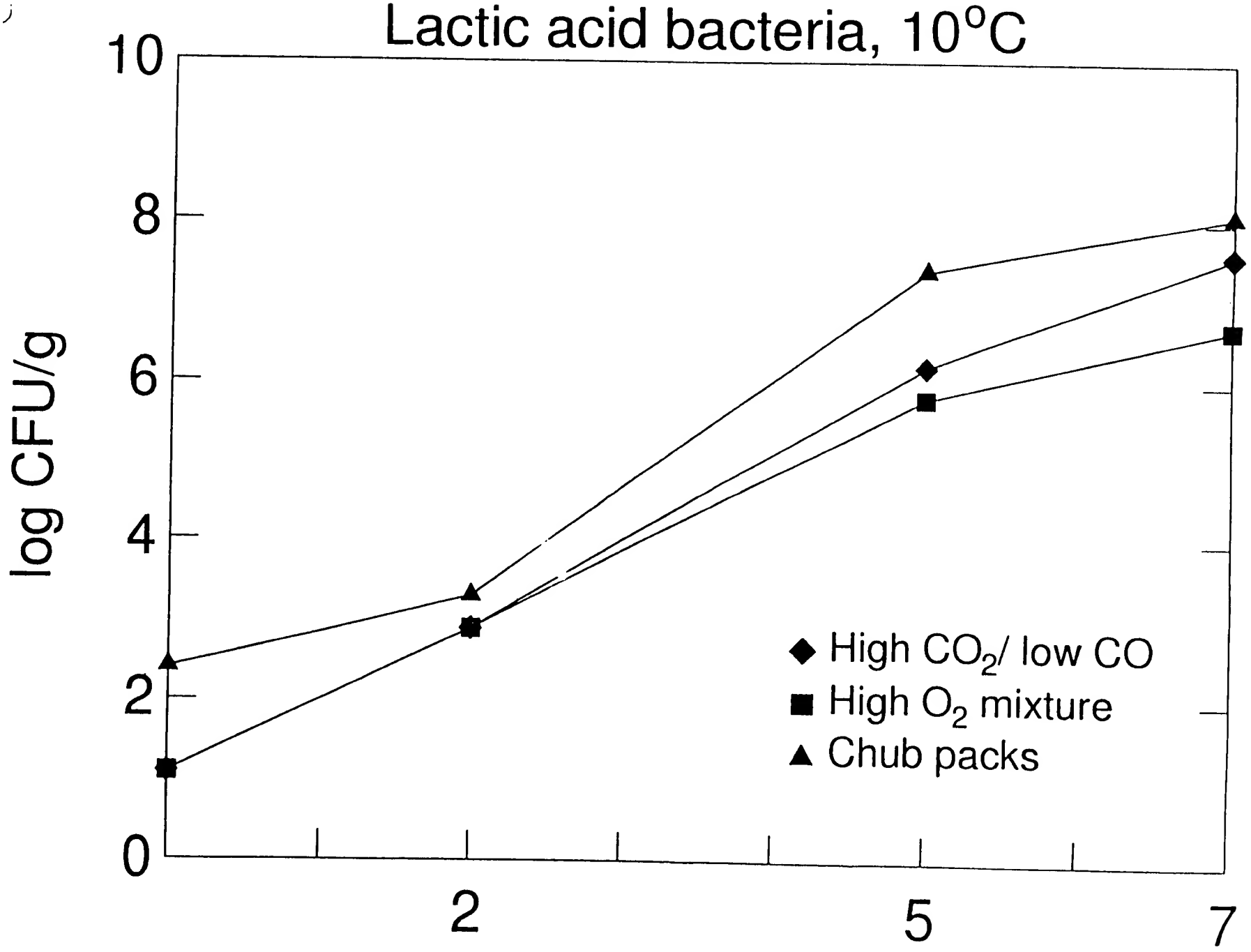

Salmonella enterica 61:K:1,5,(7)
High CO_2 / low CO
High O_2 mixture
Chub packs
log CFU/g
0
1
2
3
4
5
2
5
7

Fig 6


Lactic acid bacteria, 10°C
log CFU/g
10
8
6
4
2
0
2
5
7
High CO_2/ low CO
High O_2 mixture
Chub packs

The Use of CO as a Packaging Gas for Fresh Meat.

By Magne Yndestad

A previous report on the use of CO as a packaging gas concluded that there is unsatisfactory documentation on factors such as the development of pathogenic bacteria in the gas mixture in question (0.4% CO/60% CO_2/40% N_2). The Norwegian Research Center for Meat forwarded recent and complementary documentation on September 13, 1999.

Following scientific review, the content of this documentation can be summed up as follows:

Bacteriological Conditions

Numerous studies have been undertaken regarding trial storage involving concentrations of CO_2 in a range consistent with the "Norwegian" mixture (60-75% CO_2). Moreover, there are articles documenting the bactericidal effect of various other concentrations of gas mixtures containing CO_2. The conclusion to these trials is the following:

The low CO concentration (<0.5 CO) has no apparent effect on bacterial flora in products packaged with gas. This also holds true for N_2 (filler gas).

Concentrations of CO_2 below 5% may stimulate the growth of certain types of bacteria. Between 5 and 50%, we see an approximately linear inhibiting effect. This effect is somewhat significant, since the inhibition of growth of the sensitive flora is as much as 50% at 10% CO_2. The documented effect of CO_2 in high concentrations primarily applies to the psychrotrophic flora, including the most important spoilage bacteria.
As for the pathogenic bacteria, scientific literature in general points to the same tendency, i.e. inhibition of growth at both 4°C and higher temperatures (e.g. 10° C).
In comparison to other packaging methods or gas mixtures used, the mixture in question seems favorable both in terms of storage life and in terms of the relevant pathogens.

Following the last round of applications, The Norwegian Research Center for Meat has performed a relatively extensive study on freshly ground meat packaged in 0.3-0.5% CO/60-70% CO_2 and 30-40% N_2. Various pathogens, such as *E.coli* O157:H7, *Listeria monocytogenes*, and *Yersinia enterocolitica* were tested in this trial. The Research Center has evaluated factors such as the important possibility that the strong suppression of the general psychotrophic flora may favor certain pathogens, which will not be inhibited to the same degree. The main conclusion, however, is that the aforementioned pathogens are inhibited both at 4°C and 10°C. Comparing the CO packaging method to packaging employing a high concentration of O_2 or vacuum, shows that the risk for growth of the applied pathogens is identical or lower when packaging with CO.

The Research Center has studied the circumstances concerning salmonella bacteria and the gas mixture in question in the same products. Since none of the cultures grew at +4°C, studies were only undertaken at 10°C.
In this case, storage with packaging gas containing CO performed worst with regard to *S. dublin*, *S. enteritidis* and *S.diarizonae*, as a relatively strong growth occurred following Day 2. *S. typhimurium* too had considerable growth, although "sausage" packaging scored lower.

Bruk av CO som pakkegass til ferskt kjøtt.

av Magne Yndestad

I en tidligere utredning om bruk av CO som pakkegass ble det konkludert med at det forelå noe mangelfull dokumentasjon på blant annet utvikling av patogene bakterier i den aktuelle gassblanding (0,4% CO/60% CO_2/40% N_2). Fagsenteret for kjøtt har den 13. september -99 oversendt ny og utfyllende dokumentasjon.

Etter en faglig gjennomgang kan innholdet i dokumentasjonen oppsummeres slik:

Bakteriologiske forhold

Det foreligger en rekke arbeider som omhandler lagringsforsøk med CO_2 konsentrasjoner i det aktuelle området for den «norske» blandingen (60-75% CO_2). Det foreligger også artikler som dokumenterer den bakteriehemmende effekten av ulike andre konsentrasjoner av CO_2 gassblandinger. Konklusjonen på disse forsøkene er:

Den lave konsentrasjonen av CO (<0,5 CO) synes ikke å ha noen innvirkning på bakteriefloraen i gasspakkede produkter, det samme kan sies om N_2 (fyllgass).

CO_2 konsentrasjoner under 5% kan stimulere vekst av visse grupper av bakterier. Mellom 5 og 50% ser man en tilnærmet lineær hemmende effekt. Denne effekten er tildels betydelig, således er hemmingen i veksten på den sensitive floraen hele 50% ved 10% CO_2.
Den dokumenterte effekten av CO_2 i høye konsentrasjoner omfatter først og fremst den psykrotrofe floraen herunder de viktigste bedervelsesbakteriene.
Når det gjelder de patogene bakteriene ser man ved litteraturgjennomgang generelt sett den samme tendensen, nemlig en hemming i vekst ved både 4°C og høyere temperaturerer (for eksempel 10°C).
Sammenligner man med andre pakkemetoder/andre brukte gassblandinger synes den omsøkte blandingen å komme gunstig ut både når det gjelder holdbarhet og med hensyn til aktuelle patogener.

Etter forrige søknadsrunde har «Fagsenteret for kjøtt» utført et relativt omfattende forsøk med fersk hakket kjøtt pakket i 0,3-0,5% CO/60-70% CO_2 og 30-40% N_2. Ulike patogener som *E.coli* O157:H7, *Listeria monocytogenes* og *Yersinia enterocolitica* ble testet i forsøket.
Fagsenteret har her blant annet vurdert det viktige forholdet at det kan tenkes at den sterke undertrykkelsen av den generelle psyktrofe flora kanskje vil favorisere enkelte patogene, som ikke hemmes like mye. Hovedkonklusjonen er imidlertid at de nevnte patogener hemmes både ved 4°C og 10°C. Ved å sammenligne CO-pakkemetoden ved pakking i høg O_2 eller vakuum er risikoen for oppvekst av de anvendte patogener lik eller lavere ved CO-pakking.

Fagsenteret har også undersøkt forholdene omkring salmonellabakterier og den aktuelle gassblanding i samme produkter. Da ingen av stammene vokste ved +4°C ble det bare utført forsøk ved 10°C.
Her kom pakkegass med CO dårligst ut ved lagring når det gjaldt *S.dublin*, *S.enteritidis* og *S.diarizonae* idet en etter dag 2 fikk en relativt kraftig oppvekst. Også *S.typhimurium* vokste godt selv om «Snabb»-pakking kom dårligere ut.

This is completely in line with what is known about a whole range of salmonella bacteria in foods, i.e. that they hold up very well when competing with other bacteria, and also grow very well at temperatures around 8-10°C.
These facts emphasize the importance of cooling regardless of what packaging method is chosen.

Sensorial Circumstances
The last report pointed to the particular fact that the CO packaged meat could retain a fresh red color for days after spoilage set in. Hence, the consumer cannot *see* whether the meat he or she buys is spoiled, as opposed to fresh meat packaged in other types of gas packaging.
The Research Center notes that when opening a package, the consumer will detect any spoilage odor, and hence not eat the product. This may be true, but it is a fact that many people won't react to any incipient decay when the products looks completely "fresh." However, the packaging method for which approval is sought is meant for fresh meat that will be treated with heat prior to use. This is an additional safety factor that is important in a comprehensive evaluation.

Conclusion
The first bacteriological/sanitary statement made was based on the documentation available at the time. The new data and other relevant information from scientific literature indicate that there is sufficient evidence that the use of CO as a packaging gas as described in the application won't result in any increased risk of transmittal of food-borne diseases among consumers.

Dette er helt i samsvar med det man vet om en rekke typer av salmonellabakterier i næringsmidler, nemlig at de klarer seg meget bra i konkurranse med andre bakterier, samtidig med at de vokser svært godt ved temperaturer omkring 8-10°C.
Nevnte forhold understreker betydning av kjøling uansett hvilken pakkemetode man velger.

Sensoriske forhold

Den forrige utredningen pekte på det spesielle forhold at kjøttet i CO-pakningen kunne ha en frisk rødfarge i flere dager etter inntrådt bedervelse. En forbruker kan altså ikke se om det kjøttet vedkommende kjøper er bedervet i motsetning til hva som er tilfelle med ferskt kjøtt pakket i andre gasspakninger.
Fagsenteret anfører at en ved åpning av en pakke vil merke eventuell bedervelseslukt og derfor ikke spise produktet. Dette er nok riktig, men det er en kjennsgjerning at en del mennesker reagerer mindre på begynnende bedervelse når produktet ser helt «ferskt ut».
Pakkemetoden det søkes godkjennelse for gjelder imidlertid ferskt kjøtt som skal varmebehandles før kjøttet anvendes. Dette gir en ekstra sikkerhetsfaktor som er viktig ved en helhetsvurdering.

Konklusjon

Den første bakteriologisk/hygieniske uttalelsen som ble avgitt var basert på den dokumentasjon en da hadde til rådighet.
Ved gjennomgang av nye tilsendte data og andre relevante opplysninger fra faglitteraturen, finner en det tilstrekkelig dokumentert at bruk av CO som pakkegass som beskrevet i søknaden, ikke vil medføre øket risiko for matbårne sykdommer hos konsumentene.

[Handwritten:]
From the report "Fresh Meat in Consumer Packaging" with modified gas containing CO_2 [illegible]

IV. Report by Tore Aune: "Fresh Meat in Consumer Packaging – A Toxicological Evaluation of the Use of up to 0.5% CO in a Gas Mixture."

IV. **Rapport fra Tore Aune: "Ferskt kjøtt i forbrukerpakning - en toksikologisk vurdering av bruk av CO med opptil 0,5% av gassblanding"**

FRESH MEAT IN CONSUMER PACKAGING – A TOXICOLOGICAL EVALUATION OF THE USE OF UP TO 0.5% CO IN A GAS MIXTURE

By Tore Aune

Carbon monoxide (CO) is a colorless gas that is primarily generated by incomplete combustion of organic material. The background concentration of CO in the atmosphere is approximately 0.01-0.09mg/m^3 (0.009-0.08 ppm), while the concentration in larger cities may excede 50mg/m^3 as an 8 hour mean, depending on traffic.

(= 45 ppm = .0045 %. FW gas = 100x greater)

General Health Effects

CO attaches to the iron of the hemoglobin in the red blood cells during generation of carboxyhemoglobin (COHb), and can thus affect the transport of oxygen in the blood and the supply of oxygen to the tissues. Compared to its affinity to oxygen, hemoglobin has approximately 240 times greater affinity to CO. CO also attaches to myoglobin, cytochromes, and some other enzymes, but these reactions are considered less important than the formation of carboxyhemoglobin (WHO 1979). The health impact on humans is mainly restricted to effects on the cardiovascular system, the nervous system, and certain types of proteins and cells in the bloodstream, as well as effects on embryos (SFT 1992).

The carboxyhemoglobin percentage (COHb %) is a function of the CO concentration in the inhaled air, the exposure time and the level of physical activity (Coburn et al., 1965) (see Table 1). A CO exposure resulting in a COHb concentration above 2% in the bloodstream of the most sensitive individuals (cardiovascular patients) has been shown to give symptoms of localized oxygen deficit and chest pains. Reduced work capacity occurs at a somewhat higher COHb%, and persons suffering from angina can tolerate less strain before an attack occurs. No health effects have been detected in healthy adults at COHb concentrations below 5%.

Table 1: Blood carboxyhemoglobin percentage as a function of CO concentration in air, exposure time and different degrees of physical activity (Coburn et al., 1965):

Exposure		COHb%		
CO Conc.	Time in Hours:	At rest	Moderate Activity	Strenuous Activity
10 mg/m^3	8	1.3	1.4	1.4
25 mg/m^3	1	1.0	1.5	2.0
40 mg/m^3	1	1.3	2.2	2.9

FERSKT KJØTT I FORBRUKERPAKNING - EN TOKSIKOLOGISK VURDERING AV BRUK AV CO MED OPPTIL 0.5% AV GASSBLANDING

Av Tore Aune

Karbonmonoksid (CO) er en fargeløs gass som stort sett stammer fra ufullstendig forbrenning av organisk materiale. Bakgrunnskonsentrasjonen av CO i atmosfæren er ca. 0,01-0,09 mg/m^3 (0,009-0,08 ppm), mens konsentrasjonen i storre byer kan overskride 50 mg/m^3 som 8-timers middel, avhengig av biltrafikken.

Helseeffekter, generelt

CO binder seg til hemoglobinets jern i de røde blodlegemene under dannelse av karboksyhemoglobin (COHb), og kan derved påvirke oksygentransporten i blodet og tilførselen av oksygen til vevene. Hemoglobin har ca. 240 ganger større affinitet til CO, sammenlignet med affiniteten til oksygen. CO binder seg også til myoglobin, cytokromer og noen andre enzymer, men disse reaksjonene betraktes som mindre viktige enn dannelsen av karboksyhemoglobin (WHO 1979). Helseeffektene hos mennesker begrenser seg stort sett til effekter på hjerte-karsystemet, nervesystemet, og visse typer proteiner og celler i blodet, samt på foster (SFT 1992).

Karboksyhemoglobin-prosenten (COHb-%) er en funksjon av CO-konsentrasjonen i innåndingsluften, eksponeringstiden og nivået av fysisk aktivitet (Coburn et al., 1965) (se tabell 1). En CO-eksponering som resulterer i en COHb-konsentrasjon på over 2% i blodet hos de mest mottagelige personer (hjerte-kar pasienter) har gitt tegn på lokal oksygenmangel og brystsmerter. Ved noe høyere COHb% inntrer nedsatt arbeidskapasitet, og hjertekrampepasienter tåler mindre belastning før anfall inntreffer. Hos friske, voksne mennesker er det ikke påvist helseeffekter ved lavere COHb-konsentrasjoner enn 5%.

Tabell 1: Karboksyhemoglobin-prosenten i blodet som funksjon av CO-konsentrasjonen i luft, eksponeringstiden og ulik grad av fysisk aktivitet (Coburn et al., 1965):

Eksponering		COHb%		
CO-konc.	Tid,timer	I hvile	Moderat aktivitet	Tungt arbeid
10 mg/m^3	8	1,3	1,4	1,4
25 «	1	1,0	1,5	2,0
40 «	1	1,3	2,2	2,9

CO attachment to the hemoglobin is reversible. The half-life at ventilation at rest is approximately 4.5 hours.

A small amount of CO is continually formed in the body as a result of the decomposition of substances such as hemoproteins. This results in a COHb% of approximately 0.5. The uptake of CO through inhalation comes in addition to that. The average COHb level in non-smokers is estimated at 1.2-1.5%, while the level is 3-4% in smokers.

Survey of Health Effects Associated with CO Exposure

The negative health effects of CO are due to the fact that CO competes with oxygen for points of attachments on the hemoglobin molecule. Moreover, the release of oxygen in the tissues is reduced (WGHO 1987). Myoglobin is closely related to hemoglobin. It stores oxygen and promotes the diffusion of oxygen to muscle cells. In cardiac and skeletal muscles, myoglobin binds CO with an affinity that is 30-50 times higher than the corresponding affinity for oxygen. No reported studies have shown that the binding of CO to myoglobin can cause any health effect at a COHb level of 4-5%.

Uptake and liberation of CO occur at a relatively slow pace (hours), which means that short-time exposure to elevated CO levels will not result in any noticeable increase in the COHb level. SFT report No. 92/16 (1992) includes an overview of the correlation between blood COHb levels and health effects (Table 2).

Table 2: Correlation between blood carboxyhemoglobin levels and health effects (SFT 1992):

COHb%	Observed Effects in Humans:
50 and above	Unconsciousness, lethal when untreated.
30 and above	Headache, dizziness, nausea, and vomiting.
10 and above	May be lethal to cardiovascular patients. Headache in healthy individuals.
5 and above	Reduction of peak oxygen consumption under strenuous activity in healthy individuals.
5 and above	Impaired vision, learning ability and fine motor response.
5 and above	Exposure during pregnancy may affect the embryo.
2.9 and above	Individuals suffering from angina can tolerate less strain before an attack occurs.
2.3 and above	Reduced capacity for physical work, especially stamina.
2 and above	Possible reduced ability to concentrate and pay attention.
2 and above	Symptoms of localized oxygen deficit and incipient chest pains in cardiac patients.

The literature in the field does not seem to indicate that health effects have been proven in healthy adults exposed to CO resulting in a blood COHb concentration of less than 5%.

Bindingen av CO til hemoglobinet er reversibel. Halveringstiden ved utluftning under hvile er omtrent 4 1/2 time.

En liten mengde CO dannes kontinuerlig i kroppen som resultat av nedbrytning av bl.a. hemoproteiner. Dette resulterer i en COHb% på ca. 0,5. Opptaket av CO gjennom innånding kommer i tillegg. Gjennomsnittlig COHb-nivå hos den ikke-røykende del av befolkningen ligger på 1,2-1,5%, mens den hos røykere ligger rundt 3-4%.

Oversikt over helseeffekter assosiert med CO-eksponering

CO's helseskadelige virkninger skyldes at CO konkurrerer med oksygen om bindingsstedene på hemoglobinmolekylet. Dessuten reduseres frisettingen av oksygen i vevene (WHO 1987). Myoglobin er nærbeslektet med hemoglobin. Det lagrer oksygen og fremmer diffusjon av oksygen til muskelceller. I hjerte- og skjelettmuskler binder myoglobin CO med en affinitet som er 30-50 ganger høyere enn tilsvarende for oksygen. Det er ikke rapportert at binding av CO til myoglobin kan forårsake noen helseeffekt ved et COHb-nivå på 4-5%.

Opptak og utskillelse av CO foregår relativt langsomt (timer), og det innebærer at kortvarig eksponering for forhøyete CO-nivåer ikke vil resultere i merkbar økning i COHb-nivået. I SFT-rapport nr. 92/16 (1992) er det gitt en oppstilling over sammenhengen mellom COHb-nivåer i blodet og helseeffekter (tabell 2).

Tabell 2: Sammenheng mellom karboksyhemoglobinnivåer i blodet og helseeffekter (SFT 1992):

COHb%:	Observerte virkninger på mennesker:
50 og høyere	Bevisstløshet, dødelig dersom man ikke behandles.
30 og høyere	Hodepine, svimmelhet, kvalme og oppkast.
10 og høyere	Kan være livstruende for hjerte- og lungepasienter. Hodepine hos andre.
5 og høyere	Reduksjon av maksimalt oksygenforbruk under anstrengelse, friske.
5 og høyere	Nedsatt synsoppfattelse, læringsevne og finmotorikk.
5 og høyere	Ved eksponering av gravide kan fosteret påvirkes.
2,9 og høyere	Hjertekrampepasienter tåler mindre belastning før anfall opptrer.
2,3 og høyere	Nedsatt fysisk arbeidskapasitet, især utholdenhet.
2 og høyere	Mulig nedsatt oppmerksomhet og konsentrasjonsevne.
2 og høyere	Tegn på lokal oksygenmangel og begynnende brystsmerter hos hjertepasienter.

Etter gjennomgang av litteraturen på området synes det ikke som om man har påvist helseeffekter hos friske, voksne mennesker som er utsatt for CO som gir mindre enn 5%

However, the data indicate that a COHb level of 2-3% may have negative effects on sick and sensitive individuals, such as people suffering from cardiovascular diseases.

Exposure to CO through the Air

With regard to CO as an air pollution factor, a team of Norwegian experts (SFT 1992) suggested air quality criteria at CO concentrations resulting in a maximum of 1.5% COHb during light physical activity (including the CO produced endogenically). The correlation between CO concentration, activity level, and exposure time in order not to exceed 1.5% blood COHb is shown in Table 3.

Table 3: Calculation of CO concentrations in the air resulting in a COHb level of 1.5%, including endogenic CO production (SFT 1992):

	CO Concentration, mg/m^3		
Exposure Time:	At Rest:	Moderate Physical Activity:	Strenuous Physical Activity:
15 min	170	80	52
30 min	86	42	29
1 hour	48	24	18
8 hours	11.5	9.2	9.2

Exposure to CO through Consumption of Fresh Meat Treated with a Gas Mixture

There is a paucity of information in scientific literature concerning exposure to CO through the consumption of fresh meat treated with a gas mixture containing CO. One of the most interesting references in this regard is a 1954 publication by A. L. Tappel et al., which is unfortunately not easily accessible. However, their work has been cited in other publications, e.g. in the study by Clark et al. (1976): Tappel et al. considered a US industrial sanitary norm for CO of 50 ppm (8 hours/day), and found that such exposure would result in a blood COHb level over a longer period of time that is approximately 14 times higher than the temporary increase caused by consumption of approximately 225 g meat, provided that the myoglobin and hemoglobin in the meat are saturated with CO, and that 100% of CO from this source is transferred to the blood of the consumer (an estimate representing a hypothetical worst-case scenario). According to the authors, such treatment of meat will thus cause only a very minor effect in comparison to what is considered the safety limit, even when assuming maximum uptake of CO. Watts et al. (1978) exposed beef to a gas containing 1% CO for 3 days, and found that this resulted in a CO saturation of approximately 30% of the myoglobin. CO was lost under such storage conditions, with a half-life of approximately 3 days. After cooking, the CO concentration in the meat decreased to

COHb i blodet. Imidlertid tyder dataene på at et COHb-nivå på 2-3% kan ha uheldige virkninger hos syke og sårbare individer i samfunnet, bl.a. de som lider av hjerte-karsykdommer.

Eksponering for CO via luften

Når det gjelder CO som en luftforurensningsfaktor, foreslo en norsk ekspertgruppe (SFT 1992) luftkvalitetskriterier ved CO-konsentrasjoner som gir maksimum 1,5% COHb under lett fysisk anstrengelse (inklusive kroppens egen CO-produksjon). Sammenhengen mellom CO-konsentrasjon, aktivitetsnivå og eksponeringstid for ikke å overskride 1,5% COHb i blodet er gjengitt i tabell 3.

Tabell 3: Beregning av CO konsentrasjoner i lufta som resulterer i COHb-nivå på 1,5%, inklusive endogen CO-produksjon (SFT 1992):

Eksponeringstid:	CO-konsentrasjon, mg/m^3		
	Hvile:	Moderat fysisk aktivitet:	Tung fysisk aktivitet:
15 min	170	80	52
30 min	86	42	29
1 time	48	24	18
8 timer	11,5	9,2	9,2

Eksponering for CO gjennom konsum av ferskt kjøtt behandlet med gassblanding

I litteraturen er det svært mangelfulle opplysninger om aktuell eksponering for CO via konsum av kjøtt behandlet med gassblandinger som inneholder CO. En av de mest interessante referansene i denne sammenheng er en publikasjon av A.L.Tappel og medarbeidere i 1954, men som dessverre er vanskelig tilgjengelig. Imidlertid er det referert fra deres arbeide i andre publikasjoner, bl.a. av Clark et al. (1976): Tappel et al. tok utgangspunkt i en yrkeshygienisk norm for CO i USA på 50 ppm (8 timer/dag), og fant at en slik eksponering vil gi et COHb-nivå i blodet i lengre tid som ligger ca. 14 ganger høyere en hva man får forbigående ved konsum av ca. 225 g kjøtt, under forutsetning av at myoglobinet og hemoglobinet i kjøttet er mettet med CO, og at 100% av CO herfra kommer over i konsumenten blod (et estimat som representerer et hypotetisk «verste tilfelle»). Derfor, sier forfatterne, vil en slik behandling av kjøtt utgjøre en meget liten effekt i forhold til hva som betraktes som sikkerhetsgrensen, selv om man antar maksimalt opptak av CO.

Watts og medarbeidere (1978) eksponerte biff for 1% CO-atmosfære i 3 dager, og fant at dette gav en CO metning på ca. 30% av myoglobinet. CO gikk tapt under ulike lagringsbetingelser, med en halveringstid på omtrent 3 dager. Etter steking sank CO-konsentrasjonen i kjøttet til

below 0.09 ppm (equivalent to approximately 0.1 mg/kg). Maximum loss after cooking (on burner at 195°C) amounted to approximately 85%.

Comparison of CO Exposure through Air and Meat (CO Treated)

There is little data available for such a comparison, but a rough overview nevertheless provides some points of reference. An adult inhales 10-20m^3 air per 24 hours (depending on the activity level). This is the equivalent of 0.42-0.84m^3 per hour (or 3.36-6.72 m^3 per 8 hours).

To stay within a maximum blood COHb level of 1.5%, the CO concentration in the air must be 24 mg/m^3 for 1 hour at moderate physical activity, at 9.2 mg/m^3 for 8 hours (according to Table 3). In comparison, the CO exposure is 0.1 mg/kg after consumption of 250 g of heated CO-treated meat that has been treated for 72 hours in a gas containing 1% CO (Watts et al., 1978). Table 4 shows a calculation of CO intake from the air and a meal of CO-treated meat.

Table 4: Comparison of CO intake from air within a range without any health impact and theoretical intake of CO through consumption of a meal of CO-treated meat:

Path of Exposure:	CO Intake, 1 hour:	CO Intake, 8 hours
Lungs (15 m^3/24 hours)	24mg x 0.625 = 15.1mg	9.2mg x 5 = 46.0mg
Meat	0.025mg	0.025 mg

For CO balance between air and blood is only achieved after a considerable period of time (hours). The absorption of gases from the intestinal canal to the blood is probably considerably less efficient than from the lungs, where the tissue allows for maximum gas exchange between the alveoli and the bloodstream. This implies that intake of CO through meat probably won't cause any demonstrable increase in the blood CO level (in the form of COHb). And at any rate, the exposure from meat is much lower (approximately one thousand times lower) than through the airways, as shown in the calculations above.

According to the Norwegian Institute of Air Research (SFT 1992), the CO concentration in larger Norwegian cities is on average between 1 and 2 mg/m^3 during the winter. Maximum hourly values have been measured to approximately 60 mg/m^3, and maximum values for 8 hours to about 40 mg/m^3.

Evaluation of Other Gases Used in Foods in the EU

EU's Research Committee on Foods (SCF) has not considered CO. However, the expert team has considered other gases (EUR 1981), such as carbon dioxide (CO_2) and nitrogen oxide (NO). In this connection, the committee employed the following evaluation method, which should be applicable for CO, as well:

under 0,09 ppm (som tilsvarer ca. 0,1 mg/kg). Maksimalt tap etter steking (plate på 195 grader C) utgjorde ca. 85%.

Sammenligning av CO-eksponering via luft og kjøtt (CO-behandlet)

Det foreligger ikke noe stort materiale for å gjennomføre en slik sammenligning, men en grov oversikt vil likevel gi visse holdepunkter. Et voksent menneske puster inn 10-20 m^3 luft hvert døgn (avhengig av bl.a. aktivitetsnivået). Dette tilsvarer 0,42-0,84 m^3 per time (eller 3,36-6,72 m^3 per 8 timer).

For å holde seg innenfor et maksimalt COHb-nivå i blodet på 1,5%, må luftkonsentrasjonen av CO i 1 time ved moderat fysisk aktivitet ligge på 24 mg/m^3, og i 8 timer på 9,2 mg/m^3 (ifølge Tabell 3). Til sammenlikning vil CO-eksponeringen etter konsum av 250 g CO-behandlet kjøtt som er behandlet i 3 døgn med i CO-atmosfære på 1% være 0,1 mg/kg etter oppvarming (Watts og medarbeidere, 1978). I tabell 4 gjengis en beregning av CO-inntak via luft og et måltid CO-behandlet kjøtt.

Tabell 4: Sammelignig av CO-inntaket via luft innenfor et nivå som ikke gir helseeffekter og teoretisk inntak av CO via konsum av et måltid CO-behandlet kjøtt:

Eksponeringsvei:	CO-inntak, 1 time:	CO-inntak, 8 timer:
Lungene (15 m^3/døgn)	24 mg x 0,625 = 15,1 mg	9,2 mg x 5 = 46,0 mg
Kjøtt	0,025 mg	0,025 mg

For CO gjelder at likevekt mellom luft og blod først oppnås etter betydelig tid (timer). Absorbsjonen av gasser fra tarmkanalen til blodet er sannsynligvis langt mindre effektiv enn fra lungene hvor vevet er utviklet for maksimal gassutveksling mellom alveolene og blodet. Dette innebærer at inntak av CO via kjøtt sannsynligvis ikke vil føre til påviselig økning av CO-nivået i blodet (som COHb). Og i alle fall er eksponeringen fra kjøtt svært mye lavere (ca. 3 tier-potenser lavere) enn via luftveiene, som vist i beregningene ovenfor.

Ifølge Norsk institutt for luftforskning (SFT 1992), er CO-konsentrasjonen i større norske byer mellom 1 og 2 mg/m^3 i gjennomsnitt om vinteren. Man har målt maksimale times-verdier på ca. 60 mg/m^3, og maksimale 8-times verdier på ca. 40 mg/m^3.

Vurdering av andre gasser brukt til næringsmidler i EU

EU's vitenskapelige komité for næringsmidler (SCF), har ikke behandlet CO. Imidlertid har ekspertgruppen behandlet andre gasser (EUR 1981), som karbondioksid (CO_2) og nitrogenoksid (NO), og i den forbindelse anvendt en vurderingsmetode som også bør kunne anvendes for CO, nemlig følgende:

CO_2: This compound is a natural product of metabolism, and people are constantly exposed to carbon dioxide from the atmosphere, food and drink. Compared to this exposure, the residual content from its use as an extraction agent is insignificant. Establishing an ADI for this compound is unnecessary. The committee considers this compound acceptable as an extraction agent. It is unnecessary to determine concentration values for the residue.

N_2O: The pharmacological and pharmacokinetic properties of this gas are well known from the extensive use of N_2O as an anaesthetic. Even though no data on residual content are available, such amounts are probably so minor that they are not hazardous to the consumer. The committee finds that it is unnecessary to establish an ADI, and considers the use of N_2O as an extraction agent acceptable.

Toxicological Evaluation of the Use of CO as a Packaging Gas for Meat

People are continually exposed to carbon monoxide, both by means of endogenic production and by inhaled air. Toxicologically, it is the amount of CO bound to the blood hemoglobin (the carboxyhemoglobin percentage) that determines any health effects. The very first effects in sensitive individuals occur at COHb concentrations from approximately 2-3%. To prevent possible health effects even in the most sensitive individuals, a team of Norwegian experts has suggested limits for CO in the air that do not result in COHb concentrations above 1.5%, including the endogenic production at 0.5%. The above-mentioned estimates indicate that even if all CO in the prepared meat is transferred to the consumer's blood, the CO concentration – even a temporary concentration – will remain well below accepted limits in air. From a health perspective, the use of CO in concentrations below 0.5-1 % for fresh meat thus represents no toxicological risk.

References:

Clark, D.S. C.P. Lentz, and L.A. Roth: "Use of carbon monoxide for extending shelf-life of prepackaged fresh beef." Can. Inst. Food Sci. Technol. J., 9, 114-117, 1976.

Coburn, R.F., R.E. Forster, and P.B. Kane: "Considerations of the physiological variables that determine the blood carboxyhemoglobin in man." J.Clin.Invest., 44, 1899-1910, 1965.

EUR. "Food Science and Techniques." Reports from the Scientific Committee on Foods (Series 11), EUR 7421, Luxembourg, 1981.

SFT, "Health and environmental effects of air pollution. Recommended air quality criteria." SFT report No. 92:16, 1992.

Watts, D.A., S.K. Wolfe., and W. D. Brown: "Fate of [^{14}C] carbon monoxide in cooked or stored ground beef samples." J.Agric. Food Chem., 26, 210-214, 1978.

CO_2: Denne forbindelsen er et naturlig stoffskifteprodukt, og mennesker utsettes konstant for karbondioksid fra atmosfæren, næringsmidler og drikkevarer. Sammenlignet med denne påvirkningen er restinnholdet fra dets anvendelse som ekstraksjonsmiddel ubetydelig. Oppstilling av en ADI for denne forbindelsen er unødvendig. Komitéen anser denne forbindelse for akseptabel som ekstraksjonsmiddel. Det er unødvendig å oppstille restkonsentrasjons-verdier.

N_2O: Denne gassens farmakologiske og farmakokinetiske egenskaper er velkjente fra den utbredte anvendelse av N_2O som bedøvelsesmiddel. Selv om der ikke er tilgjengelige data om restinnhold, vil det sannsynligvis være så lavt at det ikke er noen fare for forbrukeren. Komitéen mener at det er unødvendig å oppstille en ADI, og anser anvendelsen av N_2O som ekstraksjonsmiddel for akseptabel.

Toksikologisk vurdering av bruk av CO som pakkgass for kjott

Mennesker eksponeres kontinuerlig for karbonmonoksid, både via endogen produksjon, og via inhalasjonsluften. Toksikologisk er det mengden CO bundet til blodets hemoglobin (karboksyhemoglobin-prosenten) som er avgjørende for eventuelle helseeffekter. De aller første effekter hos sårbare personer opptrer ved COHb-konsentrasjoner fra ca. 2-3%. For å unngå mulige helseeffekter selv hos de mest sårbare, har en norsk ekspertgruppe foreslått grenseverdier for CO i luft som ikke skal resultere i COHb-konsentrasjoner over 1,5%, inklusive kroppens egen-produksjon på 0.5%.

Estimater som er gjengitt ovenfor, indikerer at selvom alt CO i det tilberedte kjøttet overføres til konsumentens blod, vil CO-konsentrasjonen, selv kortvarig, ligge svært langt under aksepterte grenseverdier i luft. Ut fra en helsemessig vurdering vil ikke anvendelse av CO i konsentrasjoner under 0,5-1% til ferskt kjott representere noen toksikologisk risiko.

Litteratur:

Clark,D.S., Lentz,C.P., and Roth,L.A.: Use of carbon monoxide for extending shelf-life of prepackaged fresh beef. Can. Inst. Food Sci. Technol. J., 9, 114-117, 1976.

Coburn,R.F., Forster,R.E., and Kane,P.B.: Considerations of the physiological variables that determine the blood carboxyhemoglobin in man. J.Clin.Invest., 44, 1899-1910, 1965.

EUR, Levnedsmidler - videnskab og teknik. Rapporter fra Den videnskapelige Komité for Levnedsmidler (Ellevte serie), EUR 7421, Luxembourg, 1981.

SFT, Virkninger av luftforurensning på helse og miljø. Anbefalte luftkvalitetskriterier. SFT-rapport nr. 92:16, 1992.

Watts,D.A., Wolfe,S.K., and Brown,W.D.: Fate of [^{14}C]carbon monoxide in cooked or stored ground beef samples. J. Agric. Food Chem., 26, 210-214, 1978.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 47097-1080WO	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US02/23869	International filing date (*day/month/year*) 23 July 2002 (23.07.2002)	(Earliest) Priority Date (*day/month/year*) 25 July 2001 (25.07.2001)
Applicant PACTIV CORPORATION		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the Report**
   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
   ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:
   ☐ contained in the international application in written form.
   ☐ filed together with the international application in computer readable form.
   ☐ furnished subsequently to this Authority in written form.
   ☐ furnished subsequently to this Authority in computer readable form.
   ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
2. ☐ **Certain claims were found unsearchable** (See Box I).
3. ☐ **Unity of invention is lacking** (See Box II).
4. With regard to the **title**,
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,
   ☐ the text is approved as submitted by the applicant.
   ☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. 2
   ☐ as suggested by the applicant. ☐ None of the figures
   ☐ because the applicant failed to suggest a figure.
   ☒ because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/23869

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A23L 1/31, 3/00,3/3418,3/3436,3/3445; A23B 4/00; B65B 31/00,55/00; B65D 81/00,81/20
US CL : 426/129,124,127,315,324,396,415,418; 53/432,434

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 426/129,124,127,315,316,324,332,396,404,410,415,418; 53/432,434

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y ✓	US 4,522,835 A (WOODRUFF et al.) 11 June 1985 (11.06.1985),column 1, line 63 to column 2, line 50 and column 4, lines 3-54.	1-12,18-31,36-39,43-50,53-59,66,68,69,74-77,80-83,85-96,102-111,116,117,121-126,129,130,142,143, 146,147,150-152
Y	WO 9633096 A1 (RAMOT UNIVERSITY AUTORITY FOR APPLIED RESEARCH AND INDUSTRIAL DEVELOPMENT LTD.) 24 October 1996 (24.10.1996), see entire document.	1,14,17-22,33,35-39,52-57,65,67-69,70,76,77,85-87,98,101-104,113,115-117,128-131,134,139,141,142, 146,147
Y ✓	US 2,930,704 A (WILLIAMS) 29 March 1960 (29.03.1960), column 2, lines 22-54.	1,7,9,21,22,27,29,37-39,46,48,56,57,69,70, 75, 131,142

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 October 2002 (07.10.2002)	29 NOV 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Robert Madsen Telephone No. (703) 308-0061

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/23869

Box III TEXT OF THE ABSTRACT (Continuation of Item 5 of the first sheet)

The technical features mentioned in the abstract do not include a reference sign between parentheses (PCT Rule 8.1(d)).

NEW ABSTRACT

A method of manufacturing a modified atmosphere package comprises supplying a first package (14) including a non-barrier portion (18) substantially permeable to oxygen. A retail cut of raw meat (26) is placed within the first package (14) and the first package (14) is sealed. A second package (12) substantially impermeable to oxygen is supplied. The first package (14) is covered with the second package (12) without sealing the second package (12) so as to create a pocket (13) between the first (14) and second (12) packages. A mixture of gases is supplied into the pocket (13). The gas mixture comprises from about 0.01 to about 0.8 vol.% carbon monoxide and at least one other gas to form a low oxygen environment so as to form carboxymyoglobin on a surface of the raw meat (26). The oxygen is removed from the pocket (13) so as to sufficiently reduce an oxygen level therin so as to inhibit or prevent the formation of metmyoglobin on the surface of the raw meat(26). The second package (12) is sealed.

PCT/US02/23869

INTERNATIONAL SEARCH REPORT

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,985,342 A (RUZEK) 16 November 1999 (16.11.1999), see entire document.	1,7,8,16,17,22,27,28, 35,38-41,46,47,51,52,57,60-65,67,70,72,73,76-79,87,93,94,100,101, 104,109,110,115-119,124,125,127,128, 131,134-139,141,142,144,146-149,153
Y	EP 0 781 242 B1 (SEALED AIR) 24 February 1999 (24.02.1999), see entire document.	1-6,13-17,22-26,32-35,38-45,51,52,57-67,70-73,76-82,84,87-92,97-101,104-108,112-123,127,128,131-153

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
RONALD B. COOLLEY
JENKENS & GILCHRIST
225 W. WASHINGTON STREET, SUITE 2600
CHICAGO, IL 60606

WRITTEN OPINION

(PCT Rule 66)

Date of Mailing *(day/month/year)*	29 MAY 2003
Applicant's or agent's file reference 47097-1080WO	REPLY DUE within 2 months/days from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US02/23869	23 July 2002 (23.07.2002)	25 July 2001 (25.07.2001)

International Patent Classification (IPC) or both national classification and IPC

IPC(7): A23L 1/31, 3/00,3/3418,3/3436,3/3445; A23B 4/00; B65B 31/00,55/00; B65D 81/00,81/20 and US Cl.: 426/129,124,127,315,324,396,415,418; 53/432,434

Applicant

PACTIV CORPORATION

1. This written opinion is the first (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2 (a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

3. **The applicant is hereby invited to reply** to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension. See rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.
For an informal communication with the examiner, see Rule 66.6

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 25 November 2003 (25.11.2003).

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Robert Madsen Jean Proctor Paralegal Specialist
Facsimile No. (703)305-3230	Telephone No. (703) 308-0061

WRITTEN OPINION

International application No.
PCT/US02/23869

I. Basis of the opinion

1. With regard to the **elements** of the international application:*

☒ the international application as originally filed

☒ the description:
pages 1-27, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

☒ the claims:
pages 28-43, as originally filed
pages NONE, as amended (together with any statement) under Article 19
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

☒ the drawings:
pages 1-27, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

☐ the sequence listing part of the description:
pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination(under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages NONE _____

☐ the claims, Nos. NONE _____

☐ the drawings, sheets/~~fig~~ NONE _____

5. ☐ This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed."*

WRITTEN OPINION

International application No.
PCT/US02/23869

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. STATEMENT

Novelty (N)	Claims	NONE	YES
	Claims	1-153	NO
Inventive Step (IS)	Claims	NONE	YES
	Claims	1-153	NO
Industrial Applicability (IA)	Claims	1-153	YES
	Claims	NONE	NO

2. CITATIONS AND EXPLANATIONS
Please See Continuation Sheet

WRITTEN OPINION

International application No.
PCT/US02/23869

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

WOODRUFF et al. are silent in teaching just CO and CO_2 in the modified atmosphere. However, VERBRUGGEN teaches preserving meat color with carbon dioxide and carbon monoxide after vacuum treatment (English Abstract). Therefore it would have been obvious to modify the gas composition of WOODRUFF et al. to contain only CO and CO_2 since one would have been substituting one modified atmosphere composition for another for the same purpose.

Claims 38-49,51-56,76-86, 116-130,146-153 lack an inventive step under PCT Article 33(3) as being obvious over WOODRUFF et al. (US 4522835) in view of KOCH et al (US 3459117) and STOCKLEY III et al. (US 5686127).

Regarding claims 38-49,51,52,54-56,76-86, 116-128,130,146-153 WOODRUFF et al. teach treating storing meat in a reduced oxygen modified atmosphere of 0.1-3% CO, along with 20-60% CO_2 , 40-80% N_2 , and 0% O_2 to convert deoxymyoglobin to carboxymyoglobin on the surface of the meat wherein the O_2 is removed by flushing, evacuation, or using a scavenger (Abstract, Column 1, line 63 to Column 3, line 30) as recited in claims 43-49,53,55,56,80-83,85,86, 121-126,130,150-152. WOODRUFF et al. teach the meat remains in the modified atmosphere until ready for sale or consumption, but are silent in teaching any particular package or method of packaging for sale or consumption as recited in claims 38,76,116 and 146.

KOCH et al is relied on as evidence of the conventionality of storing meat in a reduced oxygen/modified atmosphere ***package*** for sale/consumption comprising carbon monoxide and other gases to form carboxymyoglobin (Column 1, lines 14-20,Column 3, lines 18-52).

STOCKLEY III et al. teach a reduced oxygen/modified atmosphere meat package for sale/consumption. STOCKLEY III et al. teach supplying a first polstyrene foam tray, sealing the tray with a first layer polyolefin overwrap, sealing a second layer onto the tray to form a pocket between the tray and second layer , or a pocket between the two films (i.e. with the drawstring embodiment of Figure 7) wherein the second layer is peelably removable for retailing without destroying the tray, and removing oxygen by flushing or by vacuum (Figures, Column 4, line 26 to column 6, line 5, Column 8, lines 23-31, Column 1, lines 40-62) as recited in claims 38-41,43-47,51, 52,76-80,84, 116-119,127,128,146-149,153.

Therefore, it would have been obvious to modify the reduced oxygen/modified atmosphere storage of WOODRUFF et al. and store the meat in a foam tray sealed by first layer polyolefin overwrap with a second layer sealed onto the tray to form a pocket between the tray wherein the second layer is peelably removable for retailing without destroying the tray, and removing oxygen by flushing or by vacuum since KOCH et al. teach it is known to store meat in a *package* for sale/consumption using a reduced oxygen modified atmosphere comprising carbon monoxide and STOCKLEY III et al. teach a conventional method and tray/overwrap package with a peelable layer suitable for storing meat in a reduced oxygen modified atmosphere. Thus one would have been substituting one type of storage for another for the same purpose: storage of meat for sale/consumption in a reduced oxygen modified atmosphere.

Regarding claims 53 and 129, WOODRUFF et al. teach converting deoxymyoglobin to carboxymyoglobin prior to adding the carbon dioxide mixture (column 3, lines 11-24) and requires a holding step to convert the oxymyoglobin, but are silent in teaching converting oxymyoglobin directly to carboxymyoglobin (Examples). KOCH et al. are relied on as evidence of the conventionality of converting oxymyoglobin directly to carboxymyoglobin by treating a fresh cut of meat immediately with the modified atmosphere comprising carbon dioxide without an extra holding step (Column 1, lines 14-20,Column 3, lines 18-52). Therefore to convert oxymyoglobin directly to carboxymyoglobin since by doing so one would be able to eliminate a process step (i.e. conversion the oxymyoglobin) which, when dealing with mercantile packaging process, is advantageous to save money and time.

Claim 50 lacks an inventive step under PCT Article 33(3) as being obvious over WOODRUFF et al. (US 4522835) in view of in view of KOCH et al (US 3459117) and STOCKLEY III et al. (US 5686127), further in view of VERBRUGGEN (DE1935566).

WOODRUFF et al. are silent in teaching just CO and CO_2 in the modified atmosphere. However, VERBRUGGEN teaches preserving meat color with carbon dioxide and carbon monoxide after vacuum treatment (English Abstract). Therefore it would have been obvious to modify the gas composition of WOODRUFF et al. to contain only CO and CO_2 since one would have been substituting one modified atmosphere composition for another for the same purpose.

Claims 1-153 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

---------- NEW CITATIONS ----------

/ US 5,711,978 A (BREEN et al.) 27 January 1998, see entire document.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

US 6,112,890 A (COLOMBO) 5 Septmeber 2000, see entire document.
DE 1,935,566 A (VERBRUGGEN) 18 July 1968, see English abstract.
US 3,459,117 A (KOCH et al.) 21 July 1967, see entire document.
US 5,686,127 A (STOCKLEY, III et al.) 11 November 1997, see entire document.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

TIME LIMIT:
The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

V. 2. Citations and Explanations:
Claims 1-11, 13-15,18-30,32-34,36,37,57-61,63,64,66-75,87-99,102-114,131-135,137,138,140-144 lack an inventive step under PCT Article 33(3) as being obvious over WOODRUFF et al. (US 4522835) in view of BREEN et al. (US 5711978)

WOODRUFF et al. teach treating storing meat in a modified atmosphere of 0.1-3% CO, along with 20-60% CO_2 , 40-80% N_2 , and 0% O_2 to convert deoxymyoglobein or oxymyoglobin, depending on the amount of oxygen removal prior to adding the modified atmosphere, to carboxymyoglobin on the surface of the meat wherein the O_2 is removed by flushing, evacuation, or suing a scavenger (Column 1, line 63 to Column 3, line 30) as recited in claims 2,5-11,18-21,23,25-30,36,37,58,66,68,69,71,74,75,88,91-96,102,103,105,107-111,132,140,143. WOODRUFF et al. teach the meat remains in the modified atmosphere until ready for sale or consumption, but are silent in teaching any particular package or method of packaging for sale or consumption as recited in claims 1, 22,57,70,87,104,131, and 142.

BREEN et al. teach the conventional reduced oxygen/modified atmosphere meat package for sale/consumption. BREEN et al. supplying a first polystyrene tray, sealed with a plastic overwrap, surrounding the tray with a bag, which may include an oxygen scavenger to remove oxygen, wherein the bag can be removed for retailing without destroying the tray , removing oxygen and supplying a mixture of gases into the bag, and sealing the bag (Figure 7, Column 2, lines 27-62, Column 5, lines 33-45) as recited in claims 1,3,4,13-15,22,24,32-34,57,59-61,63,64,67,70,72,87,89,90,97-99,104,106,112-114,131,133-135,137,138, and 141-144. Therefore it would been obvious to modify WOODRUFF et al. and include a conventional modified atmosphere package and packaging procedure since one would have been substituting one means/method to maintain meat in a low oxygen modified atmosphere until sale/consumption for another.

Claims 16,17,35,45,46,62,65,73,100,101,115,136,139,145 lack an inventive step under PCT Article 33(3) as being obvious over WOODRUFF et al. (US 4522835) in view of BREEN et al. (US 5711978), further in view of COLOMBO (US 6112890).

WOODRUFF et al. are silent in teaching a foam tray and a PVC or polyolefin overwrap. COLOMBO teaches a conventional modified atmosphere meat packaging comprising a tray and a bag surrounding the tray, wherein the tray is foam and is sealed with a pvc overwrap (Example 1). Therefore it would have been obvious to modify WOODRUFF et al. and include a foam tray and pvc overwrap, since one would have been substituting one type of meat tray and overwrap packaging for another for the same purpose: modified atmosphere meat packaging.

Claims 12 and 31 lack an inventive step under PCT Article 33(3) as being obvious over WOODRUFF et al. (US 4522835) in view of BREEN et al. (US 5711978), further in view of VERBRUGGEN (DE1935566)

(2-ethylthio) ethyl phosphorothioates) in or on the same raw agricultural commodity the total amount of such pesticides shall not yield more residue than that permitted by the larger of the two tolerances, calculated as demeton.

2. Section 120.105 is amended by adding thereto tolerances for residues of demeton in or on sugar beet tops and sugar beets. As amended § 120.105 reads as follows:

§ 120.105 Tolerances for residues of demeton.

Tolerances for residues of demeton (a mixture of *O,O*-diethyl *O*(and *S*)-2-(ethylthio) ethyl phosphorothioates) are established as follows:

12 parts per million in or on alfalfa hay, clover hay.

5 parts per million in or on almond hulls, fresh alfalfa, fresh clover, sugar beet tops.

1.25 parts per million in or on grapes, hops.

0.75 part per million in or on almonds, apples, apricots, broccoli, brussels sprouts, cabbage, cauliflower, celery, cottonseed, grapefruit, lemons, lettuce, muskmelons, oranges, peaches, pears, peas, pecans, peppers, plums (fresh prunes), potatoes, strawberries, tomatoes, walnuts.

0.5 part per million in or on sugar beets.

0.3 part per million in or on beans.

B. The Commissioner of Food and Drugs, having evaluated the data submitted in a petition filed by Chemagro Corporation, P.O. Box 4913, Kansas City 20, Missouri, and other relevant material, has concluded that the following regulation should issue with respect to residues of the food additive demeton present in dehydrated sugar beet pulp. Such residues have been shown to occur from application of the pesticide to sugar beets under agricultural uses provided for by a concurrent regulation under section 408 of the act. Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec. 409(c)(4), 72 Stat. 1786; 21 U.S.C. 348(c)(4)), and under the authority delegated to the Commissioner by the Secretary of Health, Education, and Welfare (25 F.R. 8625), the food additive regulations (21 CFR Part 121) are amended by adding to Subpart C the following new section:

§ 121.221 Demeton.

A tolerance of 5 parts per million is established for residues of demeton (a mixture of *0,0*-diethyl *0*(and *S*)-2-(ethylthio)ethyl phosphorothioates) in dehydrated sugar beet pulp for livestock feed when present therein as a result of the application of the pesticide in the production of sugar beets, provided that if residues of *0,0*-diethyl *S*-2-(ethylthio) ethyl phosphorodithioate are also present, the total of both residues shall not exceed 5 parts per million.

Any person who will be adversely affected by the foregoing order may at any time prior to the thirtieth day from the date of its publication in the FEDERAL

ng Clerk, De-
on, and Wel-

are Room 5240, 330 Independence Ave. SW., Washington 25, D.C., and may file objections thereto. Objections shall show wherein the person filing will be adversely affected by the order, and specify with particularity the provisions of the order deemed objectionable and the grounds for the objections. If a hearing is requested, the objections must state the issues for the hearing. A hearing will be granted if the objections are supported by grounds legally sufficient to justify the relief sought. Objections may be accompanied by a memorandum or brief in support thereof. All documents shall be filed in quantuplicate.

Effective date. This order shall be effective on the date of its publication in the FEDERAL REGISTER.

(Secs. 408(d)(2), 409(c)(4); 68 Stat. 512, 72 Stat. 1786; 21 U.S.C. 346a(d)(2), 348(c)(4))

Dated: July 26, 1961.

[SEAL] GEO. P. LARRICK,
Commissioner of Food and Drugs.

[F.R. Doc. 61-7270; Filed, Aug. 1, 1961; 8:50 a.m.]

PART 121—FOOD ADDITIVES

Subpart C—Food Additives Permitted in Animal Feed and Animal Feed Supplements

O,O-DIETHYL *S*-2-(ETHYLTHIO) ETHYL PHOSPHORODITHIOATE

Pursuant to sections 409 and 701 of the Federal Food, Drug, and Cosmetic Act and under the authority delegated to the Commissioner of Food and Drugs by the Secretary of Health, Education, and Welfare (25 F.R. 8625), § 121.215 of the food additive regulations (26 F.R. 2595) is revised to read as follows:

§ 121.215 *O,O*-Diethyl *S*-2-(ethylthio) ethyl phosphorodithioate.

A tolerance of 5 parts per million is established for residues of *O,O*-diethyl *S*-2-(ethylthio) ethyl phosphorodithioate, calculated as demeton, in dehydrated sugar beet pulp for livestock feed when present therein as a result of the application of the pesticide to the growing agricultural crop, provided that, if residues of demeton are also present, the total of both residues shall not exceed 5 parts per million.

This amendment does not require notice and public procedure since it is made for the purpose of bringing § 121.215 into conformity with the pesticide regulations.

Effective date. This order shall be effective on the date of its publication in the FEDERAL REGISTER.

(Secs. 409, 701; 52 Stat. 1055, 72 Stat. 1785; 21 U.S.C. 348, 371)

Dated: July 26, 1961.

[SEAL] GEO. P. LARRICK,
Commissioner of Food and Drugs.

[F.R. Doc. 61-7272; Filed, Aug. 1, 1961; 8:50 a.m.]

PART 121—FOOD ADDITIVES

Subpart D—Food Additives Permitted in Food for Human Consumption

COMBUSTION PRODUCT GAS

The Commissioner of Food and Drugs, having evaluated the data submitted by th Vitagen Corporation, 354 South Spring Street, Los Angeles 13, California, and other relevant material, has concluded that the following food additive regulation should issue with respect to the food additive combustion product gas used for the displacing and removal of oxygen in processing and packing of food. Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec. 409(c)(1), 72 Stat. 1786; 21 U.S.C. 348(c)(1)), and under the authority delegated to the Commissioner by the Secretary of Health, Education, and Welfare (25 F.R. 8625), the food additive regulations (21 CFR 121) are amended by adding to Subpart D the following new section:

§ 121.1060 Combustion product gas.

The food additive combustion product gas may be safely used in the processing and packaging of the foods designated in paragraph (c) of this section for the purpose of removing and displacing oxygen in accordance with the following prescribed conditions:

(a) The food additive is manufactured by the controlled combustion in air of butane, propane, or natural gas. The combustion equipment shall be provided with an absorption-type filter capable of removing possible toxic impurities through which all gas used in the treatment of food shall pass; and with suitable controls to insure that any combustion products failing to meet the specifications provided in this section will be prevented from reaching the food being treated.

(b) The food additive meets the following specifications:

(1) Carbon monoxide content not to exceed 4.5 percent by volume.

(2) The ultraviolet absorbance in isooctane solution in the range 255 millimicrons to 310 millimicrons not to exceed one-third of the standard reference absorbance when tested as described in paragraph (e) of this section.

(c) It is used or intended for use to displace or remove oxygen in the processing, storage, or packaging of citrus products, vegetable fats and vegetable oils, coffee, and wine.

(d) To assure safe use of the additive, in addition to the other information required by the act, the label or labeling of the combustion device shall bear adequate directions for use to provide a combustion product gas that complies with the limitations prescribed in paragraph (b) of this section, including instructions to assure proper filtration.

(e) The food additive is tested for compliance with paragraph (b)(2) by the following empirical method:

Spectrophotometric measurements. All measurements are made in an ultraviolet spectrophotometer in optical cells of 5 centimeters in length, and in the range of 255 millimicrons to 310 millimicrons, under the same instrumental conditions. The standard reference absorbance is the absorbance at

Aug. 2, 1961
26 FR 6918-9

[illegible] ethyl phosphorothioate) in or on the same raw agricultural commodity, the total amount of such pesticides shall not yield more residue than that permitted by the larger of the two tolerances, calculated as demeton.

2. Section 120.105 is amended by adding thereto tolerances for residues of demeton in or on sugar beet tops and sugar beets. As amended § 120.105 reads as follows:

§ 120.105 Tolerances for residues of demeton.

Tolerances for residues of demeton (a mixture of *O,O*-diethyl *O*(and *S*)-2-(ethylthio) ethyl phosphorothioates) are established as follows:

12 parts per million in or on alfalfa hay, clover hay.

5 parts per million in or on almond hulls, fresh alfalfa, fresh clover, sugar beet tops.

1.25 parts per million in or on grapes, hops.

0.75 part per million in or on almonds, apples, apricots, broccoli, brussels sprouts, cabbage, cauliflower, celery, cottonseed, grapefruit, lemons, lettuce, muskmelons, oranges, peaches, pears, peas, pecans, peppers, plums (fresh prunes), potatoes, strawberries, tomatoes, walnuts.

0.5 part per million in or on sugar beets.

0.3 part per million in or on beans.

3. The Commissioner of Food and Drugs, having evaluated the data submitted in a petition filed by Chemagro Corporation, P.O. Box 4913, Kansas City 20, Missouri, and other relevant material, has concluded that the following regulation should issue with respect to residues of the food additive demeton present in dehydrated sugar beet pulp. Such residues have been shown to occur from application of the pesticide to sugar beets under agricultural uses provided for by a concurrent regulation under section 408 of the act. Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec. 409(c)(4), 72 Stat. 1786; 21 U.S.C. 348(c)(4)), and under the authority delegated to the Commissioner by the Secretary of Health, Education, and Welfare (25 F.R. 8625), the food additive regulations (21 CFR Part 121) are amended by adding to Subpart C the following new section:

§ 121.221 Demeton.

A tolerance of 5 parts per million is established for residues of demeton (a mixture of *0,0*-diethyl *0*(and *S*)-2-(ethylthio)ethyl phosphorothioates) in dehydrated sugar beet pulp for livestock feed when present therein as a result of the application of the pesticide in the production of sugar beets, provided that if residues of *0,0*-diethyl *S*-2-(ethylthio) ethyl phosphorodithioate are also present, the total of both residues shall not exceed 5 parts per million.

Any person who will be adversely affected by the foregoing order may at any time prior to the thirtieth day from the date of its publication in the FEDERAL REGISTER file with the Hearing Clerk, Department of Health, Education, and Welfare, Room 4034, 330 Independence Avenue SW., Washington 25, D.C., written objections thereto. Objections shall show wherein the person filing will be adversely affected by the order and specify with particularity the provisions of the order deemed objectionable and the grounds for the objections. If a hearing is requested, the objections must state the issues for the hearing. A hearing will be granted if the objections are supported by grounds legally sufficient to justify the relief sought. Objections may be accompanied by a memorandum or brief in support thereof. All documents shall be filed in quantuplicate.

Effective date. This order shall be effective on the date of its publication in the FEDERAL REGISTER.

(Secs. 408(d)(2), 409(c)(4); 68 Stat. 512, 72 Stat. 1786; 21 U.S.C. 346a(d)(2), 348(c)(4))

Dated: July 26, 1961.

[SEAL] GEO. P. LARRICK,
Commissioner of Food and Drugs.

[F.R. Doc. 61-7270; Filed, Aug. 1, 1961; 8:50 a.m.]

PART 121—FOOD ADDITIVES

Subpart C—Food Additives Permitted in Animal Feed and Animal Feed Supplements

O,O-DIETHYL *S*-2-(ETHYLTHIO) ETHYL PHOSPHORODITHIOATE

Pursuant to sections 409 and 701 of the Federal Food, Drug, and Cosmetic Act and under the authority delegated to the Commissioner of Food and Drugs by the Secretary of Health, Education, and Welfare (25 F.R. 8625), § 121.215 of the food additive regulations (26 F.R. 2595) is revised to read as follows:

§ 121.215 *O,O*-Diethyl *S*-2-(ethylthio) ethyl phosphorodithioate.

A tolerance of 5 parts per million is established for residues of *O,O*-diethyl *S*-2-(ethylthio) ethyl phosphorodithioate, calculated as demeton, in dehydrated sugar beet pulp for livestock feed when present therein as a result of the application of the pesticide to the growing agricultural crop, provided that, if residues of demeton are also present, the total of both residues shall not exceed 5 parts per million.

This amendment does not require notice and public procedure since it is made for the purpose of bringing § 121.215 into conformity with the pesticide regulations.

Effective date. This order shall be effective on the date of its publication in the FEDERAL REGISTER.

(Secs. 409, 701; 52 Stat. 1055, 72 Stat. 1785; 21 U.S.C. 348, 371)

Dated: July 26, 1961.

[SEAL] GEO. P. LARRICK,
Commissioner of Food and Drugs.

[F.R. Doc. 61-7272; Filed, Aug. 1, 1961; 8:50 a.m.]

PART 121—FOOD ADDITIVES

Subpart D—Food Additives Permitted in Food for Human Consumption

COMBUSTION PRODUCT GAS

The Commissioner of Food and Drugs, having evaluated the data submitted by the Vitagen Corporation, 354 South Spring Street, Los Angeles 13, California, and other relevant material, has concluded that the following food additive regulation should issue with respect to the food additive combustion product gas used for the displacing and removal of oxygen in processing and packing of food. Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec. 409(c)(1), 72 Stat. 1786; 21 U.S.C. 348(c)(1)), and under the authority delegated to the Commissioner by the Secretary of Health, Education, and Welfare (25 F.R. 8625), the food additive regulations (21 CFR 121) are amended by adding to Subpart D the following new section:

§ 121.1060 Combustion product gas.

The food additive combustion product gas may be safely used in the processing and packaging of the foods designated in paragraph (c) of this section for the purpose of removing and displacing oxygen in accordance with the following prescribed conditions:

(a) The food additive is manufactured by the controlled combustion in air of butane, propane, or natural gas. The combustion equipment shall be provided with an absorption-type filter capable of removing possible toxic impurities through which all gas used in the treatment of food shall pass; and with suitable controls to insure that any combustion products failing to meet the specifications provided in this section will be prevented from reaching the food being treated.

(b) The food additive meets the following specifications:

(1) Carbon monoxide content not to exceed 4.5 percent by volume.

(2) The ultraviolet absorbance in isooctane solution in the range 255 millimicrons to 310 millimicrons not to exceed one-third of the standard reference absorbance when tested as described in paragraph (e) of this section.

(c) It is used or intended for use to displace or remove oxygen in the processing, storage, or packaging of citrus products, vegetable fats and vegetable oils, coffee, and wine.

(d) To assure safe use of the additive, in addition to the other information required by the act, the label or labeling of the combustion device shall bear adequate directions for use to provide a combustion product gas that complies with the limitations prescribed in paragraph (b) of this section, including instructions to assure proper filtration.

(e) The food additive is tested for compliance with paragraph (b)(2) by the following empirical method:

Spectrophotometric measurements. All measurements are made in an ultraviolet spectrophotometer in optical cells of 5 centimeters in length, and in the range of 255 millimicrons to 310 millimicrons, under the same instrumental conditions. The standard reference absorbance is the absorbance

with particularity the provisions of the order deemed objectionable and the grounds for the objections. If a hearing is requested, the objections must state the issues for the hearing. A hearing will be granted if the objections are supported by grounds legally sufficient to justify the relief sought. Objections may be accompanied by a memorandum or brief in support thereof. All documents shall be filed in quintuplicate.

Effective date. This order shall be effective on the date of its publication in the FEDERAL REGISTER.

(Sec. 409(c)(1), 72 Stat. 1786; 21 U.S.C. 348(c)(1))

Dated: December 7, 1962.

GEO. P. LARRICK,
Commission of Food and Drugs.

[F.R. Doc. 62-12361; Filed, Dec. 13, 1962; 8:46 a.m.]

PART 121—FOOD ADDITIVES

Subpart D—Food Additives Permitted in Food for Human Consumption

COMBUSTION PRODUCT GAS

The Commissioner of Food and Drugs, having evaluated the data submitted in petitions filed by the Whirlpool Corporation, Benton Harbor, Michigan, and the Vitagen Corporation, 1263 Westwood Boulevard, Los Angeles, California, and other relevant material, has concluded that the food additive regulation with respect to combustion product gas should be amended as set forth below. Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec. 409(c)(1), 72 Stat. 1786; 21 U.S.C. 348(c)(1)), and under the authority delegated to the Commissioner by the Secretary of Health, Education, and Welfare (25 F.R. 8625), § 121.1060(c) (21 CFR 121.1060; 27 F.R. 4014) is amended to read as follows:

§ 121.1060 Combustion product gas.

* * * * *

(c) It is used or intended for use to displace or remove oxygen in the processing, storage, or packaging of beverage products and other food, except fresh meats.

Any person who will be adversely affected by the foregoing order may at any time within 30 days from the date of its publication in the FEDERAL REGISTER file with the Hearing Clerk, Department of Health, Education, and Welfare, Room 5440, 330 Independence Avenue SW., Washington 25, D.C., written objections thereto. Objections shall show wherein the person filing will be adversely affected by the order and specify with particularity the provisions of the order deemed objectionable and the grounds for the objections. If a hearing is requested, the objections must state the issues for the hearing. A hearing will be granted if the objections are supported by grounds legally sufficient to justify the relief sought. Objections may be accompanied by a memorandum or brief in support thereof. All documents shall be filed in quintuplicate.

Effective date. This order shall become effective on the date of its publication in the FEDERAL REGISTER.

(Sec. 409(c)(1), 72 Stat. 1786; 21 U.S.C. 348(c)(1))

Dated: December 7, 1962.

GEO. P LARRICK,
Commissioner of Food and Drugs.

[F.R. Doc. 62-12360; Filed, Dec. 13, 1962; 8:46 a.m.]

Title 39—POSTAL SERVICE

Chapter I—Post Office Department

PART 168—DIRECTORY OF INTERNATIONAL MAIL

Individual Country Amendments

The regulations of the Post Office Department in § 168.5 *Individual country regulations* are amended as follows:

I. In country "Bolivia", under Parcel Post, amend the item "Prohibitions" to read as follows:

Prohibitions. Firearms, daggers, blackjacks, brass knuckles, sidearms and concealable weapons.

Cigarette lighters.

Gambling devices.

Pharmaceutical and medicinal products, unless approved by the Bolivian health authorities. In case of doubt, senders should ascertain from the addressees in advance of mailing whether the medicine they desire to send will be admitted.

Articles which violate the Bolivian trademark laws.

Counterfeit or illegal currency; advertisements imitating currency or postage stamps, except for philatelic or numismatic catalogs.

Adulterated or harmful beverages or foodstuffs.

II. In country "Canada", as amended by 27 F.R. 404, 27 F.R. 10369, under Parcel Post, the item "Prohibitions" is amended by revising the sixth paragraph to include "Plumage and skins of wild birds" and by adding a new paragraph at the end thereof to prescribe regulations for importing meat. As so amended, paragraph six and the new paragraph read as follows:

Prohibitions. * * *

Commercial tags of metal. Prison-made goods being sold or intended for sale by a person or firm. Plumage and skins of wild birds.

* * * * *

Meat and meat food products, unless federally inspected and passed and marked accordingly. If intended for sale, export certification by the United States Department of Agriculture is also required. Meat or meat food product for personal use is exempt from export certification, but the addressee is required to certify to the Canadian authorities that it will not be offered for sale in Canada.

III. In country "Japan", under Parcel Post, the item "Prohibitions" is amended by revising the second paragraph to include wool samples among animal or hoofed animals. As so amended, the second paragraph reads as follows:

Prohibitions. * * *

The following must be accompanied by official inspection certificates showing that they are free from domestic animals' infectious disease: Meat, bones, skin, hair, feathers, horns or hoofs of hoofed animals, rabbits, or poultry, wool samples, poultry eggs for hatching; honey bees.

IV. In country "Kenya and Uganda", as amended by 27 F.R. 3738, 27 F.R. 5659, under Parcel Post, amend the tabular information immediately following the item "Air parcel rates" by striking out "Weight limit: 11 pounds", and inserting in lieu thereof "Weight limit: 22 pounds."

V. In country "Laos", as amended by 27 F.R. 8592, amend the item "Observations" where it appears both under Postal Union Mail and Parcel Post, to respectively read as follows:

Observations. The following are the only post offices in operation:

Vientiane.	Paksé.
Honeisai.	Paksong.
Luangprabang.	Khongsedoné.
Sayaboury.	Champassak.
Paksane.	Muong Kong.
Khammouane.	Saravane.
Savannakhet.	Attopeu.

* * * * *

Observations. See the item "Observations" under Postal Union Mail for post offices which are in operation.

VI. In country "Tanganyika Territory" under Parcel Post, amend the tabular information immediately following the item "Air parcel rates" by striking out "Weight limits: 11 pounds" and inserting in lieu thereof "Weight limits: 22 pounds".

VII. In country "Thailand", as amended by 27 F.R. 7022, under Parcel Post, make the following changes to show that insured parcel post service is available.

A. Amend the tabular information immediately following the item "Air parcel rates" to read as follows:

Weight limit: 22 pounds
Sealing: Insured parcels must, and ordinary parcels may be sealed
Registration: No
Insurance: Yes
Postal forms required:
1 Form 2922
1 Form 2966

B. Strike out the item "*Indemnity.* No provision." and insert in lieu thereof the following:

Insurance. The following insurance fees and limits of indemnity apply:

Limit of indemnity:	Fee, cents
Not over $10	20
From $10.01 to $25	25
From $25.01 to $50	35
From $50.01 to $100	55

Insured parcels may only be addressed to Bangkok or Dhonburi.

Print on the wrapper, near the "INSURED" endorsement and number, the amount for which the parcel is insured. This amount shall be shown in United

MEMORANDUM OF CONFERENCE

May 22, 1962

BETWEEN: Mr. Donald W. Thomas, Legal Counsel, The Whirlpool Corporation
Benton Harbor, Michigan

and

Mr. A. T. Spiher, Jr., Food Additive Petitions Control Branch

SUBJECT: Combustion product gas.
Food Additive Petition 751.

Mr. Thomas called without previous appointment to discuss the above petition. He said that he had received my letter of May 10, 1962, in which we filed the petition, and said that we may need additional data on meat. These data would be needed to establish that the treatment of meat would not serve to cause the meat to retain its fresh red color longer than meat not so treated.

I explained to Mr. Thomas the way in which petitions are handled, and explained the question which we have concerning possible deception of the consumer where treatment of the meat leads to longer retention of the fresh red color. I said that they could either submit additional data on this point or they could request withdrawal of the portion of the petition for meat, and explained the different courses of action.

Mr. Thomas said that they had data concerning the retention of red col r in meat, and they will get it together. He was concerned, however, about whether he should submit this as an amendment which would start the time clock over, or should withdraw animal products from the petition, to submit later on.

I said that this was a decision which he would have to make in the light of the explanation we had given him, and I suggested that he submit the data which they have and let us look at it before they did anything additional, because what they had done might be sufficient for our people.

I further suggested that when he submit the information for meat, he should supplement the data in the petition to explain exactly how the combustion product gas is to be used on the various commodities named in their petition. He said that he would do so. Briefly, he said that the gas was to be used as the atmosphere in a cold storage room.

In response to a question, he said that they had tested the effluent from their generat r and were satisfied that the gas complied with the requirements establi hed in the food additive regulation.

cc: FA DF DP BE DOM BPS
ATSpiher:nrg:5/25/62
D/D:ATS:nrg:5/24/62

Alan T. Spiher, Jr.

Whirlpool
CORPORATION

ADMINISTRATIVE CENTER • BENTON HARBOR, MICHIGAN

July 23, 1962

Mr. Alan T. Spiher, Jr.
Food and Drug Administration
Department of Health, Education and Welfare
Washington 25, D. C.

1A 3/9/62

Subject: Food Additive Petition No. 751

Dear Mr. Spiher:

We are in receipt of your letter of May 10, 1962, advising us of the filing of Food Additive Petition No. 751 with an effective filing date of March 24, 1962.

In view of your comments in the above-mentioned letter, we now request that our petition as originally presented be amended so as to delete any reference to animal products wherein paragraph 121.1060, section (c) of Part 121, Sub-Part D of Title 21 would now read as follows:

> (c) It is used or intended for use to displace or remove oxygen in the processing, storage, or packaging of citrus products, vegetable fats and vegetable oils, coffee, wine, fruit and fruit products and vegetable and vegetable products.

The following comments are submitted to further supplement the Remarks section of our first letter of March 6, 1962.

In food studies conducted at the Whirlpool Research Laboratories involving the use of combustion product gas as set forth in paragraph 121.1060 of Title 21, fruits and vegetables were stored under refrigeration at temperatures between

DF DP 7/13/62

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JUL 25 1962

32° and 45° F. and in their normal distribution containers, that is, baskets, crates and boxes. Products so stored had a shelf life of from three to five times that of air-stored food held at the same temperature. The results of one such study involving apples stored in air versus apples stored in conventional controlled atmosphere versus apples stored in combustion product gas are presented in the attached table. It will be noted that apples stored in combustion product gas had firmer flesh and a lower incidence of scald than did apples stored either in air or conventional controlled atmosphere even though the apples in combustion product gas were in storage for a longer period of time.

The combustion product gas under study at Whirlpool would most likely be used in the following general areas:

1. Fresh fruit and vegetable storage

2. Processors - storage, packaging and processing

3. Transportation

Because of these diverse applications, our petition requests approval for fruit and vegetable "products" as well as the natural, original raw fruits and vegetables.

To expand on the use of combustion product gas by food processors, the following examples are presented:

1. Storage of fruits and vegetables in order to have better quality control, improve yield and extend packaging season.

2. Packaging of processed foods in inert gases, i. e., nitrogen and/or carbon dioxide to prevent oxidative changes that may develop during storage.

3. Use of gas mixtures in certain processing steps as a "blanket" to keep out oxygen and prevent the associated undesirable changes.

We are hopeful that the requested amendment to the petition as well as the supplemental information presented above will clear up any questions concerning Food Additive Petition No. 751 and that favorable action will be shortly forthcoming.

Very truly yours,

WHIRLPOOL CORPORATION

By John E. Mahaffay
Vice President

other information required by the act, the following:

(i) The name of the additive, chloropentafluoroethane.

(ii) The percentage of the additive present in the case of a mixture.

(iii) The designation "food grade".

(2) The label or labeling of the food additive container shall bear adequate directions for use.

[42 FR 14526, Mar. 15, 1977, as amended at 43 FR 11317, Mar. 17, 1978; 43 FR 14644, Apr. 7, 1978]

§ 173.350 Combustion product gas.

The food additive combustion product gas may be safely used in the processing and packaging of the foods designated in paragraph (c) of this section for the purpose of removing and displacing oxygen in accordance with the following prescribed conditions:

(a) The food additive is manufactured by the controlled combustion in air of butane, propane, or natural gas. The combustion equipment shall be provided with an absorption-type filter capable of removing possible toxic impurities, through which all gas used in the treatment of food shall pass; and with suitable controls to insure that any combustion products failing to meet the specifications provided in this section will be prevented from reaching the food being treated.

(b) The food additive meets the following specifications:

(1) Carbon monoxide content not to exceed 4.5 percent by volume.

(2) The ultraviolet absorbance in isooctane solution in the range 255 millimicrons to 310 millimicrons not to exceed one-third of the standard reference absorbance when tested as described in paragraph (e) of this section.

(c) It is used or intended for use to displace or remove oxygen in the processing, storage, or packaging of beverage products and other food, except fresh meats.

(d) To assure safe use of the additive in addition to the other information required by the act, the label or labeling of the combustion device shall bear adequate directions for use to provide a combustion product gas that complies with the limitations prescribed in paragraph (b) of this section, including instructions to assure proper filtration.

(e) The food additive is tested for compliance with paragraph (b)(2) by the following empirical method:

Spectrophotometric measurements. All measurements are made in an ultraviolet spectrophotometer in optical cells of 5 centimeters in length, and in the range of 255 millimicrons to 310 millimicrons, under the same instrumental conditions. The standard reference absorbance is the absorbance at 275 millimicrons of a standard reference solution of naphthalene (National Bureau of Standards Material No. 577 or equivalent in purity) containing a concentration of 1.4 milligrams per liter in purified isooctane, measured against isooctane of the same spectral purity in 5-centimeter cells. (This absorbance will be approximately 0.30.)

Solvent. The solvent used is pure grade isooctane having an ultraviolet absorbance not to exceed 0.05 measured against distilled water as a reference. Upon passage of purified inert gas through some isooctane under the identical conditions of the test, a lowering of the absorbance value has been observed. The absorbance of isooctane to be used in this procedure shall not be more than 0.02 lower in the range 255 millimicrons to 310 millimicrons, inclusive, than that of the untreated solvent as measured in a 5-centimeter cell. If necessary to obtain the prescribed purities, the isooctane may be passed through activated silica gel.

Apparatus. To assure reproducible results, the additive is passed into the isooctane solution through a gas-absorption train consisting of the following components and necessary connections:

1. A gas flow meter with a range up to 30 liters per hour provided with a constant differential relay or other device to maintain a constant flow rate independent of the input pressure.

2. An absorption apparatus consisting of an inlet gas dispersion tube inserted to the bottom of a covered cylindrical vessel with a suitable outlet on the vessel for effluent gas. The dimensions and arrangement of tube and vessel are such that the inlet tube introduces the gas at a point not above 5¼ inches below the surface of the solvent through a sintered glass outlet. The dimensions of the vessel are such, and both inlet and vessel are so designed, that the gas can be bubbled through 60 milliliters of isooctane solvent at a rate up to 30 liters per hour without mechanical loss of solvent. The level corresponding to 60 milliliters should be marked on the vessel.

3. A cooling bath containing crushed ice and water to permit immersion of the absorption vessel at least to the solvent level mark.

Caution. The various parts of the absorption train must be connected by gas-tight tubing and joints composed of materials which will neither remove components from

nor add components to the gas stream. The gas source is connected in series to the flow-rate device, the flow meter, and the absorption apparatus in that order. Ventilation should be provided for the effluent gases which may contain carbon monoxide.

Sampling procedure. Immerse the gas-absorption apparatus containing 60 milliliters of isooctane in the coolant bath so that the solvent is completely immersed. Cool for at least 15 minutes and then pass 120 liters of the test gas through the absorption train at a rate of 30 liters per hour or less. Maintain the coolant bath at 0 °C throughout. Remove the absorption vessel from the bath, disconnect, and warm to room temperature. Add isooctane to bring the contents of the absorption vessel to 60 milliliters, and mix. Determine the absorbance of the solution in the 5-centimeter cell in the range 255 millimicrons to 310 millimicrons, inclusive, compared to isooctane. The absorbance of the solution of combustion product gas shall not exceed that of the isooctane solvent at any wavelength in the specified range by more than one-third of the standard reference absorbance.

§ 173.355 Dichlorodifluoromethane.

The food additive dichlorodifluoromethane may be safely used in food in accordance with the following prescribed conditions:

(a) The additive has a purity of not less than 99.97 percent.

(b) It is used or intended for use, in accordance with good manufacturing practice, as a direct-contact freezing agent for foods.

(c) To assure safe use of the additive:

(1) The label of its container shall bear, in addition to the other information required by the act, the following:

(i) The name of the additive, dichlorodifluoromethane, with or without the parenthetical name "Food Freezant 12".

(ii) The designation "food grade".

(2) The label or labeling of the food additive container shall bear adequate directions for use.

§ 173.357 Materials used as fixing agents in the immobilization of enzyme preparations.

Fixing agents may be safely used in the immobilization of enzyme preparations in accordance with the following conditions:

(a) The materials consist of one or more of the following:

(1) Substances generally recognized as safe in food.

(2) Substances identified in this subparagraph and subject to such limitations as are provided:

Substances	Limitations
Acrylamide-acrylic acid resin: Complying with § 173.5(a)(1) and (b) of this chapter.	May be used as a fixing material in the immobilization of glucose isomerase enzyme preparations for use in the manufacture of high fructose corn syrup, in accordance with § 184.1372 of this chapter.
Cellulose triacetate	May be used as a fixing material in the immobilization of lactase for use in reducing the lactose content of milk.
Diethylaminoethyl-cellulose	May be used as a fixing material in the immobilization of glucose isomerase enzyme preparations for use in the manufacture of high fructose corn syrup, in accordance with § 184.1372 of this chapter.
Dimethylamine-epichlorohydrin resin: Complying with § 173.60(a) and (b) of this chapter.	May be used as a fixing material in the immobilization of glucose isomerase enzyme preparations for use in the manufacture of high fructose corn syrup, in accordance with § 184.1372 of this chapter.
Glutaraldehyde	Do.
Periodic acid (CAS Reg. No. 10450-60-9)..	

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

Food and Drug Administration
Washington, DC 20204

Eric Greenberg
Ungaretti and Harris
3500 Three First National Plaza
Chicago, IL, 60602-4405

Re: GRAS Notice No. GRN 000083

Dear Mr. Greenberg:

The Food and Drug Administration (FDA) is responding to the notice, dated August 29, 2001, that Ungaretti and Harris submitted on behalf of Pactiv Corporation (Pactiv) in accordance with the agency's proposed regulation, proposed 21 CFR 170.36 (62 FR 18938; April 17, 1997; Substances Generally Recognized as Safe (GRAS)). FDA received the notice on September 4, 2001, and designated it as GRAS Notice No. GRN 000083.

The subject of the notice is carbon monoxide (CO). The notice informs FDA of the view of Pactiv Corporation (Pactiv) that CO is GRAS, through scientific procedures, for use as a component of a gas mixture in a modified atmosphere packaging (MAP) system. The level of CO in this MAP system is 0.4 percent. The other components of the MAP system are carbon dioxide (30 percent) and nitrogen (69.6 percent). The MAP system would be used for packaging fresh cuts of case ready muscle meat and ground case ready meat to maintain wholesomeness, provide flexibility in distribution, and reduce shrinkage of the meat. The case ready meats would be removed from the MAP system prior to retail display.

As part of its notice, Pactiv includes letters from a panel of individuals (Pactiv's GRAS panel) who evaluated the data and information that are the basis for Pactiv's GRAS determination. Pactiv considers the members of its GRAS panel to be qualified by scientific training and experience to evaluate the safety of substances added to food. Pactiv's GRAS panel evaluated information and data on the chemical identity, manufacture and processing, conditions of proposed use, and estimated daily intakes of CO used in a MAP system for meat. Pactiv's GRAS panel also evaluated studies (published and unpublished) of the effects of CO used in a MAP system for meat. Members of the GRAS panel reviewed and evaluated the publicly available information summarized in the GRAS notice. Based on the data and information reviewed, Pactiv's GRAS panel concludes that CO, when produced in accordance with current good manufacturing practice and meeting appropriate food grade specifications, is GRAS, through scientific procedures under the conditions of its intended use.

The notice describes publicly available information pertaining to the identity and characteristic properties of CO. Carbon monoxide (Chemical Abstracts Service Registry Number 630-08-0) is a colorless, odorless, gas. The notice includes a list of properties of CO and identifies the

manufacturer who currently supplies CO to Pactiv. Pactiv intends to use CO at a minimum purity of 99.99 percent ("commercial grade"). Pactiv includes a list of specifications for CO with limits on the levels of other gases and considers CO of this purity to be "food grade."

The notice describes information about existing regulations and notices regarding food substances that contain CO as a significant component:

- Wood smoke, which includes CO as a component, is permitted by regulation as an ingredient in meat and poultry products under regulations issued by the U.S. Department of Agriculture (9 CFR 318.7(c)(4), 381.147(e)(4) and 424.21(c)).

- Combustion product gas, which includes CO as a component at a maximum level of 4.5 percent by volume, is approved for use in the production of beverages and other foods (except fresh meat) under FDA's regulations (21 CFR 173.350).

- Tasteless smoke, which includes CO as a primary component, is the subject of GRN 000015 for use on raw tuna, before it is frozen, to preserve its taste, aroma, texture, and color. In response to GRN 000015, FDA had no questions regarding the notifier's conclusion that tasteless smoke is GRAS under the intended conditions of use.

The notice describes the estimated consumption of CO per meal as a consequence of its intended use as a component in a MAP system for storing meat. Assuming that 30 percent of the CO present in the MAP is absorbed into the meat and that there is an 85 percent reduction of CO due to cooking the meat, Pactiv calculates a realistic intake estimate to be 0.084 milligrams (mg) CO per meal. Pactiv also calculates a worst case intake estimate to be 1.88 mg CO per meal, assuming that 100 percent of the CO present in the MAP is absorbed into the meat and that there is no reduction in CO during cooking. Pactiv cites published articles to support the assumptions used in the realistic exposure estimate and to support the conclusion that exposure to CO is safe at this level.

The notice describes published reports of studies demonstrating the technical effect and safety of using CO as a component of a MAP system (similar to the MAP system that is the subject of GRN 000083) for storing meat. These reports include published data (microbial growth profiles and odor and color data) from meat stored in MAP containing CO, CO_2, and N_2, and meat stored in MAP containing only CO_2 and N_2. Pactiv concludes that the presence of CO in MAP systems allows the meat to maintain a desirable red color during storage. In addition, CO neither affects the ability of the MAP system to slow the growth of a variety of microorganisms, nor affects the characteristic odor of meat spoilage.

The notice describes an unpublished study using the MAP system that is the subject of GRN 000083. The study examined the effects of the system on initial meat color, stability of color during display, and the relationship between color deterioration and microbial growth. The notice also includes unpublished pictures that compare the ageing (color deterioration) of meats stored for 20 days in an environment of CO, CO_2, and N_2, to the ageing of fresh cut meat and the ageing of meat stored in a high oxygen environment. From these data, Pactiv concludes that once meat is removed from a MAP system containing CO, its color deteriorates at a similar rate to

that f meat that has not been exposed to CO. Pactiv also concludes that the use of CO in a MAP system does not result in red color life extension that could mask microbial spoilage of the meat.

Based on the information provided by Pactiv, as well as other information available to FDA, the agency has no questions at this time regarding Pactiv's conclusion that CO is GRAS under the intended conditions of use. The agency has not, however, made its own determination regarding the GRAS status of the subject use of CO. As always, it is the continuing responsibility of Pactiv to ensure that food ingredients that the firm markets are safe, and are otherwise in compliance with all applicable legal and regulatory requirements.

During its evaluation of GRN 000083, OFAS consulted with the Labeling and Consumer Protection Staff of the Food Safety and Inspection Service (FSIS) of the United States Department of Agriculture regarding the use of CO in meat products. Based on the information submitted by Pactiv, FSIS has concluded that the MAP system (ActiveTech™ 2001) as described in Pactiv's notice, and used under the conditions stated in Pactiv's notice, would be acceptable for packaging red meat cuts and ground meat. In FSIS' view, Pactiv has demonstrated that this MAP system complies with FDA's definition of a processing aid that appears in labeling regulations (21 CFR 101.100(a)(3)). There is no lasting functional effect in the food and there is an insignificant amount of carbon monoxide present in the finished product under the proposed conditions of use. As such, similar to uses of other MAP gases (e.g., nitrogen), there are no labeling issues in regard to meat cuts and ground meat packaged using this MAP. Additionally, when considering the use of a food ingredient or additive in a meat product, FSIS historically has treated each livestock species separately. However, in this case, the data submitted by Pactiv can be extrapolated to all species of livestock. If you have any additional questions, you should direct your inquiry to Dr. Robert Post, Director, Labeling and Consumer Protection Staff, Office of Policy, Program Development and Evaluation, Food Safety and Inspection Service, 300 12th Street, SW, Room 602, Washington, DC 20250-3700. The telephone number of his office is (202) 205-0279 and the FAX number is (202)205-3625.

In accordance with proposed 21 CFR 170.36(f), a copy of the text of this letter, as well as a copy of the information in your notice that conforms to the information in proposed 21 CFR 170.36(c)(1), is available for public review and copying on the homepage of the Office of Food Additive Safety (on the Internet at http://www.cfsan.fda.gov/~lrd/foodadd.html).

Sincerely,

Alan M. Rulis, Ph.D.
Director
Office of Food Additive Safety
Center for Food Safety
and Applied Nutrition